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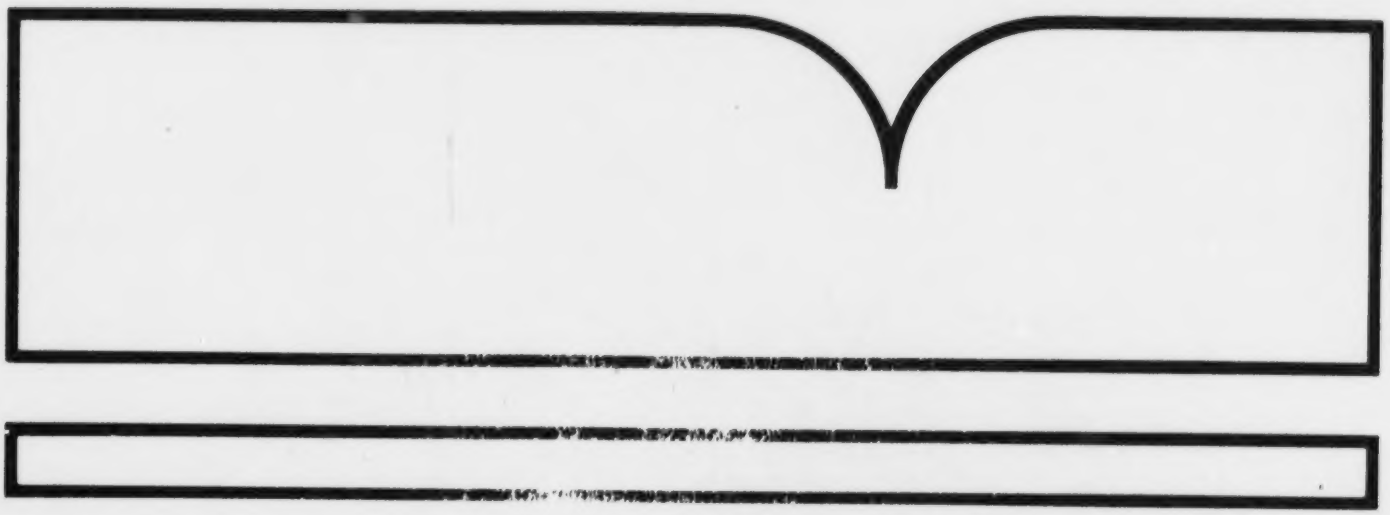

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ANALYSIS OF MATHEMATICAL MODELS FOR POLLUTANT TRANSPORT AND DISSIPATION

by

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Four realistic nonlinear models of pollutant transport with turbu-diffusion and reaction in rivers were studied. Exact solutions for all the kinetics models (no transport and no diffusion--the so-called stirred tank reactor) are described. An algorithm for calculating the rate constants from the exact solution is given.

Exact solutions for all systems also are provided when transport terms are included with the kinetics (the plug flow model). The inclusion of turbulent diffusion prevents exact solution, but the methods or perturbation and the maximum (minimum) principle provide approximate solutions and bounds on the travelling wave solutions. The steady state is also analyzed by the bounding technique. These bounds, which may be used independently, demonstrate how the various parameters affect the solutions.

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management or engineering tools to help pollution control officials achieve water quality goals through watershed management.

Complex mathematical models are increasingly used in studies of the movement, transformation and impact of pollutants in rivers and streams. For most studies, exact solutions are given for, at most, simplified or linearized problems whereas the true physical system is nonlinear. In recognition of this, four more sophisticated nonlinear mathematical models have been developed.

David W. Duttweiler
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ABSTRACT

Four realistic nonlinear models of pollutant transport with turbulent diffusion and reaction in rivers were studied. Exact solutions for all the kinetics models (no transport and no diffusion--the so-called stirred tank reactor) are described. An algorithm for calculating the rate constants from the exact solution is given.

Exact solutions for all systems also are provided when transport terms are included with the kinetics (the plug flow model). The inclusion of turbulent diffusion prevents exact solution, but the methods of perturbation and the maximum (minimum) principle provide approximate solutions and bounds on the travelling wave solutions. The steady state is also analyzed by the bounding technique. These bounds, which may be used independently, demonstrate how the various parameters affect the solutions.

This report was submitted in fulfillment of Contract No. 807114010 by the Georgia Institute of Technology under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 15 August 1978 to 7 October 1980, and work was completed as of 7 October 1980.

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NOTATION

$\hat{C}_1, \hat{C}_2, \hat{C}_3$ - concentrations of pesticide, bacteria and organic carbon

D_i - diffusion coefficients

k_i - rate constants

$\bar{v}$ - mean stream velocity

τ - time

$\bar{x}$ - distance

K - Constant in Model III, IV (Monod) kinetics

$\alpha, \beta, \gamma, \delta$ - scaling parameters (see individual cases)

L - length(of river)

$N_{Pe}^{(i)} = \frac{L\bar{v}}{D_i}$ - Peclet number for mass transfer

t - dimensionless time (see individual cases)

x - dimensionless distance (see individual cases)

C_1, C_2, C_3 - scaled concentrations

E_i - constants of integration and material balance.

$\varepsilon = k_1 K / k_3$ - in equation (40).

$R = k_3 / k_1$ - in equation (52c)

$\eta = x + t$ - in equation (53)

F(x-t), G(x-t), H(x-t), K(x-t), $\omega = x - t$ in equations (55) to (68).

f(x), g(x), h(x) - initial data for C_1, C_2, C_3

$j(t)$, $k(t)$, $m(t)$ - boundary data for C_1, C_2, C_3

$S = k_3 k_2 L / k_1 \bar{v}$

$u(x)$ - dimensionless velocity

$U(x) = \int^x \frac{d\eta}{u(\eta)}$

$\eta = x - t$ in equations (69) and beyond

$\lambda_1, \lambda_2, \lambda_3$ constants in (71).

$\beta = Npe$ - in Section 7 and beyond

$\lambda = k_3/k_1$, $\lambda = k_3 k_2 L / k_1 \bar{v}$ - Section 7 and beyond.

$C_1 = f(\eta)$

$C_2 = g(\eta)$

$C_3 = h(\eta)$, Section 7 and beyond.

$h(0) = \theta$, initial data

$f(0) = K$, in equation (87)

$h_0, h_1, \cdots$ terms in perturbation expansion

$\bar{f}, \underline{f}$ upper and lower bounds, respectively

$C_1 = p(x)$, $C_2 = q(x)$, $C_3 = r(x)$ in steady state analysis of Section 10

$A = q + r/\lambda$, in conservation law for Model I (steady state)

$A = q/\lambda_2 + r/\lambda_1$, in conservation law for Model III

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I am indebted to Dr. James Falco of the EPA Environmental Research Laboratory - Athens for many useful technical discussions. This work has much more practical importance because of them.

In addition to myself the technical staff consisted of Dr. E. Adams, an expert on Interval Analysis, who contributed greatly to Section 11; Mr. R. Lohner, a research assistant, who very ably analyzed and computed for a year; and Mr. R. Boisvert who checked a large portion of the analysis for me. I am very grateful for all of this professional assistance.

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INTRODUCTION

Recent studies (Falco and Mulkey [1], Bansal [2], Cleary [3], and Falco [4]) of direct interest to EPA's Environmental Research Laboratory - Athens (EPA - AERL) were carried out to study the movement, transformation and impact of pollutants in rivers and streams. These pollutant transport models are partial differential equations describing the concentrations of pollutants, bacteria, etc., in streams. In these models biochemical reactions are assumed to be pseudo-first order in pollutant concentration and biodegradation is assumed to follow various kinetics with Monod kinetics (see Falco and Mulkey [1] or Monod [5]) often used.

In all of the foregoing studies exact solutions are given for at most simplified and/or linearized problems whereas the true physical system is nonlinear. Numerical solutions are usually developed for such systems. While useful, numerical solutions are not easily employable in analyzing the model's adequacy and in parameter studies. Exact solutions readily permit these analyses. In addition, unless sophisticated error analysis is carried out, numerical solutions of complicated systems must be viewed with caution and even suspicion--this is especially true for nonlinear systems because of potential nonuniqueness, singularities and bifurcation possibilities (see Ames [6]).

In this report are employed four more realistic and thus more sophisticated nonlinear mathematical models of pollutant transport, turbulent diffusion and reaction in rivers and streams. These are akin to those used by Falco and Mulkey [1] and Falco [4].

The four models are described in Section 1 and dimensional analysis carried out in Section 2 for finite and infinite dimensional models. In Section 3 exact solutions for all of the kinetic models (no transport, no diffusion) - the so-called stirred tank reactor - will be given and discussed. Section 4 shows how the exact kinetic solutions may be used to calculate the rate constants. An algorithm suitable for a digital computer is given. In Section 5 the transport terms will be included - the so-called plug flow model - and all systems solved exactly. Section 6 presents some remarks concerning the full system which now includes the turbulent dispersion effects.

Travelling wave solutions for all models are discussed in detail in Section 7 and in Section 8 perturbation methods are applied to the equation for the pollutant of Models I and II. Difficulties in the perturbation analysis suggest that upper and lower bounds, involving all the parameters of the problems, will be more useful. These are constructed using the maximum (minimum) principle in Section 9 for the travelling waves and in Section 10 for the steady state.

Since the parameters are not well known it is shown in Section 11 how deferred interval analysis can be used to calculate an approximation to the range of the upper bound. A summary and conclusion closes the report.

1. MATHEMATICAL MODELS

With $\hat{C}_i$, i = 1,2,3 as the concentrations of pesticide, bacteria and organic carbon, D_i, i = 1,2,3 the respective diffusion coefficients (actually dispersion coefficients to account for turbulent mixing), k_i= 1,2,3 the appropriate rate constants and $\bar{v}$ the mean stream velocity*, the model is

$$\frac{\partial \hat{C}_1}{\partial \tau} + \bar{v} \frac{\partial \hat{C}_1}{\partial \bar{x}} = D_1 \frac{\partial^2 \hat{C}_1}{\partial \bar{x}^2} - k_1 f_1(\hat{C}_1, \hat{C}_2, \hat{C}_3) \qquad (1)$$

$$\frac{\partial \hat{C}_2}{\partial \tau} + \bar{v} \frac{\partial \hat{C}_2}{\partial \bar{x}} = D_2 \frac{\partial^2 \hat{C}_2}{\partial \bar{x}^2} + k_2 f_2(\hat{C}_1, \hat{C}_2, \hat{C}_3) \qquad (2)$$

$$\frac{\partial \hat{C}_3}{\partial \tau} + \bar{v} \frac{\partial \hat{C}_3}{\partial \bar{x}} = D_3 \frac{\partial^2 \hat{C}_3}{\partial \bar{x}^2} - k_3 f_3(\hat{C}_1, \hat{C}_2, \hat{C}_3) \qquad (3)$$

In these equations $\bar{x}$ represents distance along the river, τ is time, and $\bar{v}$ is assumed constant unless otherwise specified. Inclusion of more spatial variables is possible especially in the case of no diffusion.

Model I: Second order kinetics in all terms

$$f_1 = \hat{C}_1\hat{C}_2 \quad , \quad f_2 = \hat{C}_2\,\hat{C}_3 \quad , \quad f_3 = \hat{C}_2\,\hat{C}_3 \qquad (4)$$

* $\bar{v}$ may be a function of x (see Section 5).

Model II: Third order kinetics in first term, second order in the others.

$$f_1 = \hat{C}_1\hat{C}_2\hat{C}_3 \quad , \quad f_2 = \hat{C}_2\hat{C}_3 \quad , \quad f_3 = \hat{C}_2\hat{C}_3 \tag{5}$$

Model III: Second order kinetics in first term, Monod kinetics in the others.

$$f_1 = \hat{C}_1\hat{C}_2 \quad , \quad f_2 = \hat{C}_2\hat{C}_3/(K + \hat{C}_3) \quad , \quad f_3 = \hat{C}_2\hat{C}_3/(K + \hat{C}_3) \tag{6}$$

Model IV: Third order kinetics in first term, Monod kinetics in the others.

$$f_1 = \hat{C}_1\hat{C}_2\hat{C}_3 \quad , \quad f_2 = \hat{C}_2\hat{C}_3/(K + \hat{C}_3) \quad , \quad f_3 = \hat{C}_2\hat{C}_3/(K + \hat{C}_3) \tag{7}$$

The above formulations are included in an attempt to represent a range of kinetic and mathematical complexity. Second order formulations (I and III) are logical, standard formulations. The third order kinetics formulations (II and IV) are not yet supportable by field or laboratory evidence.

2. DIMENSIONAL ANALYSIS

When the model equations are transformed to dimensionless form there are a number of environmental benefits, in addition to the computational ones (see Kline [7] and / or Barenblatt [8] for more background).

These include

i) Reduction of the number of independent biological, chemical and physical parameters;

ii) Determination of governing independent parameters;

iii) Converting units of parameters in a systematic fashion;

iv) Guiding, generalizing and assisting in the collection of minimum amounts of data. Determination of unknown coefficients and optimum choice of variables and/or parameters for biological and physical experiments.

The procedure will be described in detail for Model I and results recorded for the other models. In addition some additional results will be presented for kinetics only, in which a search for parameter free models is fruitful for one case (Model II). The first results are for a river of finite length L.

Model I ($f_1 = \hat{C}_1\hat{C}_2$, $f_2 = \hat{C}_2\hat{C}_3$, $f_3 = \hat{C}_2\hat{C}_3$)

Let L be the river's length in some suitable units. With

$x = \bar{x}/L$, $\tau = \alpha t$, $\hat{C}_1 = \beta C_1$, $\hat{C}_2 = \gamma C_2$, $\hat{C}_3 = \delta C_3$

equations (1), (2) and (3) become, respectively,

$$\frac{\partial C_1}{\partial t} + \frac{\alpha\bar{v}}{L}\frac{\partial C_1}{\partial x} = \frac{D_1\alpha}{L^2}\frac{\partial^2 C_1}{\partial x^2} - k_1\alpha\gamma C_1 C_2 \qquad (8)$$

$$\frac{\partial C_2}{\partial t} + \frac{\alpha\bar{v}}{L}\frac{\partial C_2}{\partial x} = \frac{D_2\alpha}{L^2}\frac{\partial^2 C_2}{\partial x^2} + k_2\alpha\delta C_2 C_3 \qquad (9)$$

$$\frac{\partial C_3}{\partial t} + \frac{\alpha\bar{v}}{L}\frac{\partial C_3}{\partial x} = \frac{D_3\alpha}{L^2}\frac{\partial^2 C_3}{\partial x^2} - k_3\alpha\gamma C_2 C_3 \qquad (10)$$

With the choice $\alpha = L/\bar{v}$ all the left hand sides become parameter free and the coefficients of the second derivatives become reciprocals of the well known Peclet (see Perry (9)) numbers

$$N_{Pe}^{(i)} = \frac{L\bar{v}}{D_i}$$

for mass transfer. A further choice of $\gamma = \bar{v}/k_1 L$ changes (8) into

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = \frac{1}{N_{Pe}^{(1)}}\frac{\partial^2 C_1}{\partial x^2} - C_1 C_2 \qquad (11)$$

When the choice $\delta = \bar{v}/k_2 L$ is made equation (9) becomes

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \frac{1}{N_{Pe}^{(2)}}\frac{\partial^2 C_2}{\partial x^2} + C_2 C_3 \,, \qquad (12)$$

and equation (10) is transformed to

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = \frac{1}{N_{Pe}^{(3)}} \frac{\partial^2 C_3}{\partial x^2} - \frac{k_3}{k_1} C_2 C_3 \qquad (13)$$

Summarizing now, it is seen that the dimensionless variables are

$x = \bar{x}/L$, $t = \tau\bar{v}/L$, $C_1 = \hat{C}_1 k_1 L/\bar{v}$ (actually β is arbitrary), $C_2 = \hat{C}_2 k_1 L/\bar{v}$, $C_3 = \hat{C}_3 k_2 L/\bar{v}$ and the dimensionless equations are (11), (12) and (13). The basic dimensionless parameters are those of reaction k_3/k_1 and those of mass transfer $N_{Pe}^{(1)}$, $N_{Pe}^{(2)}$, and $N_{Pe}^{(3)}$. In many cases the D_i are all equal, say to D, because they result, primarily, from turbulent mixing. For those cases there are only <u>two</u> parameters k_3/k_1 and $N_{Pe} = L\bar{v}/D$.

<u>Model II</u> ($f_1 = \hat{C}_1\hat{C}_2\hat{C}_3$, $f_2 = \hat{C}_2\hat{C}_3$, $f_3 = \hat{C}_2\hat{C}_3$)

In this case the choice

$x = \bar{x}/L$, $t = \tau\bar{v}/L$, $C_1 = \hat{C}_1 k_1 L/\bar{v}$ (β is again an arbitrary choice), $C_2 = \hat{C}_2\, k_1/k_2$, $C_3 = \hat{C}_3 k_2 L/\bar{v}$ gives rise to the dimensionless equations

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = \frac{1}{N_{Pe}^{(1)}} \frac{\partial^2 C_1}{\partial x^2} - C_1 C_2 C_3 \qquad (14)$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \frac{1}{N_{Pe}^{(2)}} \frac{\partial^2 C_2}{\partial x^2} + C_2 C_3 \qquad (15)$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = \frac{1}{N_{Pe}^{(3)}} \frac{\partial^2 C_3}{\partial x^2} - \left[\frac{k_3 k_2 L}{k_1 \bar{v}}\right] C_2 C_3 \qquad (16)$$

As before, if the D_i are all equal, the dimensionless equations contain only <u>two</u> parameters.

<u>Model III</u> ($f_1 = \hat{C}_1\hat{C}_2$, $f_2 = \hat{C}_2\hat{C}_3/(K + \hat{C}_3) = f_3$

Here the choice of

$x = \bar{x}/L$, $t = \tau\bar{v}/L$, $C_1 = \hat{C}_1 k_1 L/\bar{v}$ (β is arbitrary), $C_2 = \hat{C}_2 k_1 L/\bar{v}$ and $C_3 = \hat{C}_3/K$ gives rise to the dimensionless equations

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = \frac{1}{N_{Pe}^{(1)}} \frac{\partial^2 C_1}{\partial x^2} - C_1 C_2 \tag{17}$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \frac{1}{N_{Pe}^{(2)}} \frac{\partial^2 C_2}{\partial x^2} + \frac{k_2 L}{\bar{v}} \frac{C_2 C_3}{1 + C_3} \tag{18}$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = \frac{1}{N_{Pe}^{(3)}} \frac{\partial^2 C_3}{\partial x^2} - \frac{k_3}{K k_1} \left[\frac{C_2 C_3}{1 + C_3}\right] \tag{19}$$

In this case, when the D_i are all equal, there are three parameters, N_{Pe}, $k_2 L/\bar{v}$ and k_3/Kk_1 in the dimensionless equations.

<u>Model IV</u> ($f_1 = \hat{C}_1\hat{C}_2\hat{C}_3$, $f_2 = \hat{C}_2\hat{C}_3/(K + \hat{C}_3) = f_3$)

Here again the choice of

$x = \bar{x}/L$, $t = \tau\bar{v}/L$, $C_1 = \hat{C}_1 k_1 LK/\bar{v}$ (β is arbitrary)

$C_2 = \hat{C}_2 k_1 LK/\bar{v}$ and $C_3 = \hat{C}_3/K$ generates the dimensionless equations

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = \frac{1}{N_{Pe}^{(1)}} \frac{\partial^2 C_1}{\partial x^2} - C_1 C_2 C_3 \tag{20}$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \frac{1}{N_{Pe}^{(2)}} \frac{\partial^2 C_2}{\partial x^2} + \frac{k_2 L}{\bar{v}} \left[\frac{C_2 C_3}{1 + C^3}\right] \tag{21}$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = \frac{1}{N_{Pe}^{(3)}} \frac{\partial^2 C_3}{\partial x^2} - \frac{k_3}{K^2 k_1} \left[\frac{C_2 C_3}{1 + C_3}\right] \tag{22}$$

As in Model III these dimensionless equations have three parameters in that case where the D_i are all equal.

Remark 1: While the foregoing dimensional analysis is the more familiar one there are alternatives. Of these only one example, for the full system of Model I, is presented. In that case where the river is arbitrarily long the following can be used. With

$x = \bar{x} \cdot \bar{v}/D_1$, $t = \tau v^2/D_1$, $C_1 = \hat{C}_1 (k_1 D_1/\bar{v}^2)$, $C_2 = \hat{C}_2 (k_1 D_1/\bar{v}^2)$

and $C_3 = \hat{C}_3 (k_2 D_1/\bar{v}^2)$ the dimensionless equations become

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = \frac{\partial^2 C_1}{\partial x^2} - C_1 C_2$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \frac{D_2}{D_1} \frac{\partial^2 C_2}{\partial x^2} + C_2 C_3$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = \frac{D_3}{D_1} \frac{\partial^2 C_3}{\partial x^2} - \frac{k_3}{k_1} C_2 C_3$$

When $D_1 = D_2 = D_3$ it is worth remarking that this dimensionless system has only <u>one</u> parameter k_3/k_1.

Remark 2: It is usually not possible to eliminate all parameters by dimensional analysis. However, in some systems a complete elimination is possible. That situation occurs in the kinetics of Model II - that is for

$$\frac{d\hat{C}_1}{d\tau} = -k_1\hat{C}_1\hat{C}_2\hat{C}_3 \tag{23}$$

$$\frac{d\hat{C}_2}{d\tau} = k_2\hat{C}_2\hat{C}_3 \tag{24}$$

$$\frac{d\hat{C}_3}{d\tau} = -k_3\hat{C}_2\hat{C}_3. \tag{25}$$

Here, with $t = (k_2k_3/k_1)\tau$, $C_1 = \hat{C}_1$, $C_2 = (k_1/k_2)\hat{C}_2$ and $C_3 = (k_1/k_3)\hat{C}_3$ the dimensionless kinetic equations become

$$\frac{dC_1}{dt} = -C_1C_2C_3$$

$$\frac{dC_2}{dt} = C_2C_3$$

$$\frac{dC_3}{dt} = -C_2C_3$$

which are parameter <u>free</u>! These cannot be compared with the classical results generated from (14), (15) and (16) because of the use of $\bar{v}$ and L in that analysis.

3. EXACT KINETIC SOLUTIONS

In this section we derive the exact solutions for all four kinetic (stirred tank reactors) systems in which diffusion ($D_i = 0$, $i = 1,2,3$) and transport ($\bar{v} = 0$) are neglected. Alternative dimensional analysis must be carried out but no details are presented for that analysis.

Model I:

In this case the kinetic equations are

$$\frac{d\hat{C}_1}{d\tau} = -k_1\hat{C}_1\hat{C}_2, \quad \frac{d\hat{C}_2}{d\tau} = k_2\hat{C}_2\hat{C}_3, \quad \frac{d\hat{C}_3}{d\tau} = -k_3\hat{C}_2\hat{C}_3.$$

With $t = k_1\hat{C}_2(0)\tau$, $C_1 = \hat{C}_1/\hat{C}_1(0)$, $C_2 = \hat{C}_2/\hat{C}_2(0)$, and $C_3 = k_2\hat{C}_3/k_1\hat{C}_2(0)$ the dimensionless equations, in one parameter, are

$$\frac{dC_1}{dt} = -C_1C_2 \tag{26}$$

$$\frac{dC_2}{dt} = C_2C_3 \tag{27}$$

and

$$\frac{dC_3}{dt} = -\frac{k_3}{k_1}C_2C_3 . \tag{28}$$

An exact solution of equations (26), (27) and (28) is obtained as a result of the following analysis. From (26) and (28), with $C_1 \neq 0$ and $C_3 \neq 0$,

$$\frac{1}{C_1}\frac{dC_1}{dt} = -C_2 = \frac{k_1}{k_3}\frac{1}{C_3}\frac{dC_3}{dt}$$

which integrates to

$$C_1(t) = E_1 C_3^{k_1/k_3}, \tag{29}$$

where E_1 is a constant of integration. From (27) and (28)

$$\frac{dC_2}{dt} = -\frac{k_1}{k_3}\frac{dC_3}{dt},$$

or

$$C_2(t) = E_2 - \frac{k_1}{k_3} C_3(t). \tag{30}$$

Finally, substituting (30) into (28), that equation becomes

$$\frac{dC_3}{dt} = -\frac{k_3}{k_1}\left(E_2 C_3 + C_3^2\right) = -E_3 C_3 + C_3^2,$$

where $E_3 = k_3 E_2/k_1$. This is a Bernoulli equation readily integrable to

$$C_3(t) = \frac{E_2}{E_2 E_4 \exp[k_3 E_2 t/k_1] + k_1/k_3} \tag{31}$$

which includes two arbitrary constants, E_2 and E_4.

From the dimensionless quantities it is clear that $C_1(0) = 1$, $C_2(0) = 1$ and $C_3(0) = \frac{k_2}{k_1}\frac{\hat{C}_3(0)}{\hat{C}_2(0)}$. To evaluate E_1, E_2 and E_4 these values are used. Thus from (29)

$$E_1 = C_1(0)/\left[C_3(0)\right]^{k_1/k_3} = \left[\frac{k_1}{k_2}\frac{\hat{C}_2(0)}{\hat{C}_3(0)}\right]^{k_1/k_3},$$

$$E_2 = 1 + \frac{k_2}{k_3}\,\frac{\hat{C}_3(0)}{\hat{C}_2(0)}\,,\quad E_4 = \frac{1}{C_3(0)} - \frac{k_1}{k_3}\,\frac{1}{E_2}\,.$$

If $C_3 = 0$ then $C_2 = \text{constant} = a$, so that $C_1(t) = \exp[-at]$.

Remark 3: Once $C_3(t)$ has been calculated from (31) the relations (29) and (30) provide exact solutions for $C_1(t)$ and $C_2(t)$. From (31) it follows that $C_3 \to 0$ as $t \to \infty$. Since $k_1/k_3 > 0$ equation (29) and and comment before Remark 3 imply that $C_1 \to 0$ also. This raises questions about this model for long time studies. Because of this, we do not show any computations but delay them for Model II.

Remark 4: Another feature of kinetic systems which is of interest in analysis is the conservation law. For these equations (26,27,28) of Model I there are two, namely

$$C_2(t) + \frac{k_1}{k_3}\,C_3(t) = \text{constant}$$

and

$$\ln C_1(t) - \frac{k_1}{k_3}\,\ln C_3(t) = \text{constant}.$$

Model II

The kinetic equations for this system are those dimensionless equations of Remark 2 of Section 2.

Integration of that system and determination of the conservation law is easily accomplished by rewriting the system as

$$\frac{d\,\ln C_1}{dt} = -C_2C_3\,,\quad \frac{dC_2}{dt} = C_2C_3,\quad \frac{dC_3}{dt} = -C_2C_3.$$

Consequently,

$$\frac{d \ln C_1}{dt} + 2 \frac{dC_2}{dt} + \frac{dC_3}{dt} = 0$$

so that the conservation law is

$$\ln C_1(t) + 2C_2(t) + C_3(t) = \text{constant}, \tag{32}$$

valid for all t. In dimensioned quantities (32) becomes

$$\ln \hat{C}_1 + 2 \frac{k_1}{k_2} \hat{C}_2 + \frac{k_1}{k_3} \hat{C}_3 = \ln \hat{C}_1(0) + 2 \frac{k_1}{k_2} \hat{C}_2(0) + \frac{k_1}{k_3} \hat{C}_3(0)$$

where $\hat{C}_i(0)$ are the initial concentrations.

The complete integration generates the results

$$C_2(t) = E_1 - C_3(t) \tag{33}$$

$$C_3(t) = \frac{E_1 E_2}{E_2 + e^{E_1 t}} \tag{34}$$

and

$$C_1(t) = E_3 \exp\left\{\frac{E_1 E_2}{E_2 + e^{E_1 t}}\right\} \tag{35}$$

$$C_2(t) = E_1/(1 + E_2 \exp(-E_1 t)) \tag{36}$$

where E_1, E_2 and E_3 are arbitrary constants evaluated from initial concentrations. Thus

$$E_1 = C_2(0) + C_3(0) = \frac{k_1}{k_2} \hat{C}_2(0) + \frac{k_1}{k_3} \hat{C}_3(0)$$

$$E_2 = \frac{\frac{k_1}{k_3} \hat{C}_3(0)}{E_1 - \frac{k_1}{k_3} \hat{C}_3(0)}, \quad E_3 = \hat{C}_1(0) \exp\left\{\frac{-E_1 E_2}{1 + E_2}\right\}$$

Remark 5: The explicit nature of these solutions permits us to study various limiting processes. For example, from (34) it is seen that $C_3 \to 0$ as $t \to \infty$ and hence $C_2 \to E_1$ in that same limit, from equation (36). Also from (35) $\lim_{t\to\infty} C_1 = E_3$. These are asymptotic or limiting results. This model has an appropriate asymptotic form.

Since the equations for Model II can be made dimensionless and parameter free, a single master curve for each variable will suffice. However, when the initial data changes, new curves must be generated because of the dimensional analysis. Curves for two initial states ($C_i(0) = 1,10$) are given as Figures 1 and 2.

Model III.

This third model uses Monod kinetics (see Monod [5]) in the second and third equation so that the system to be studied is

$$\frac{d\hat{C}_1}{d\tau} = -k_1\hat{C}_1\hat{C}_2 \ , \ \frac{d\hat{C}_2}{d\tau} = k_2\frac{\hat{C}_2\hat{C}_3}{K+\hat{C}_3} \ , \ \frac{d\hat{C}_3}{d\tau} = -k_3\frac{\hat{C}_2\hat{C}_3}{K+\hat{C}_3} \qquad (37)$$

Once again a new dimensionless set of variables must be introduced since the full system in Section 2 employed $\bar{v}$ and L. These parameters play no role here! With $t = k_2\tau$, $C_1 = \hat{C}_1/\hat{C}_1(0)$, $C_2 = \frac{k_3\hat{C}_2}{k_2K}$ and $C_3 = \hat{C}_3/K$ equations (37) become

$$\frac{dC_1}{dt} = -\frac{k_1K}{k_3}C_1C_2, \quad \frac{dC_2}{dt} = \frac{C_2C_3}{1+C_3} = -\frac{dC_3}{dt} \qquad (38)$$

To obtain the exact solution of (38) first observe that

$$C_2(t) = E_1 - C_3(t). \qquad (39)$$

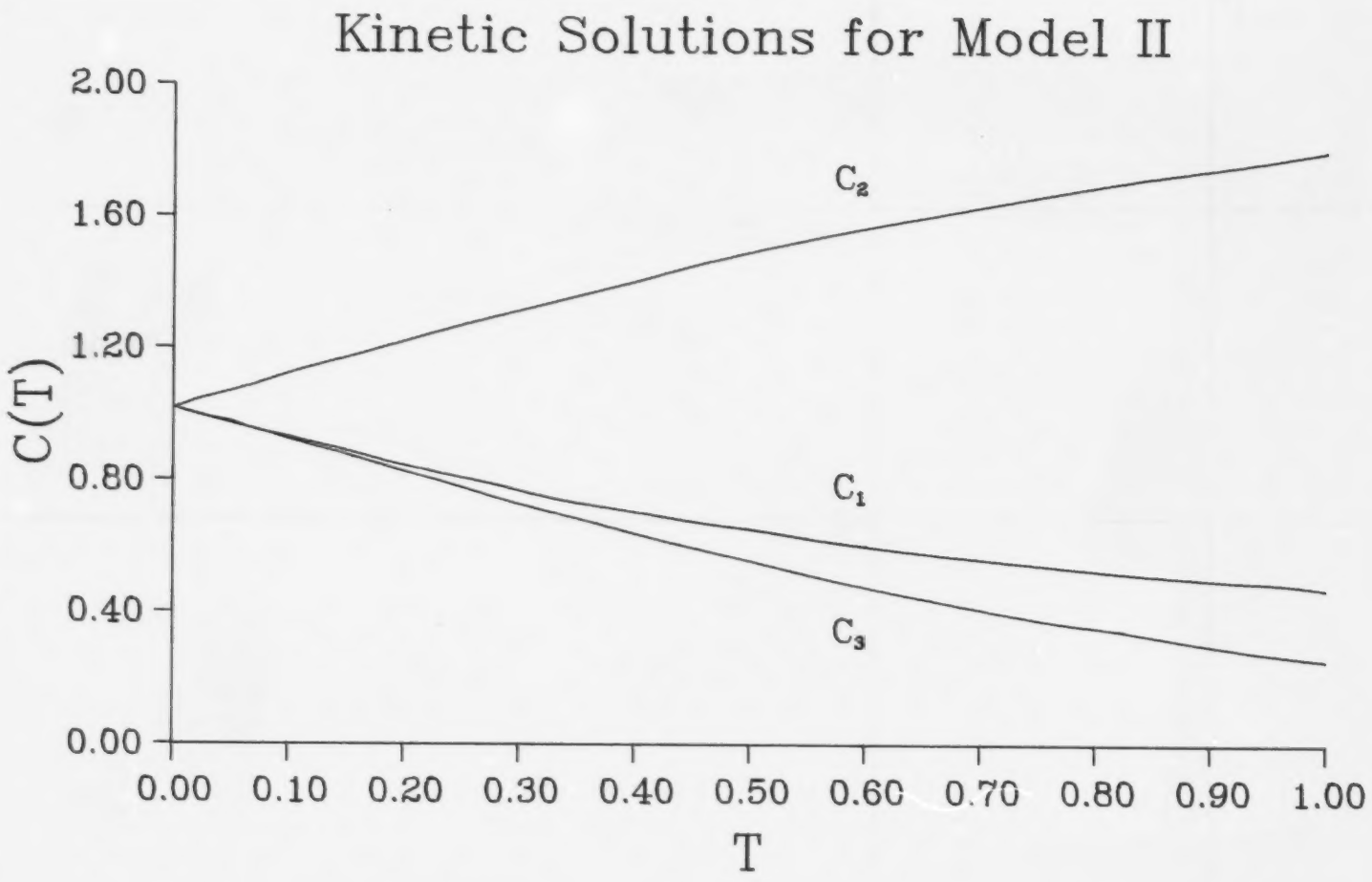

Figure 1 Dimensionless Concentrations vs Dimensionless Time $C_i(0)=1$

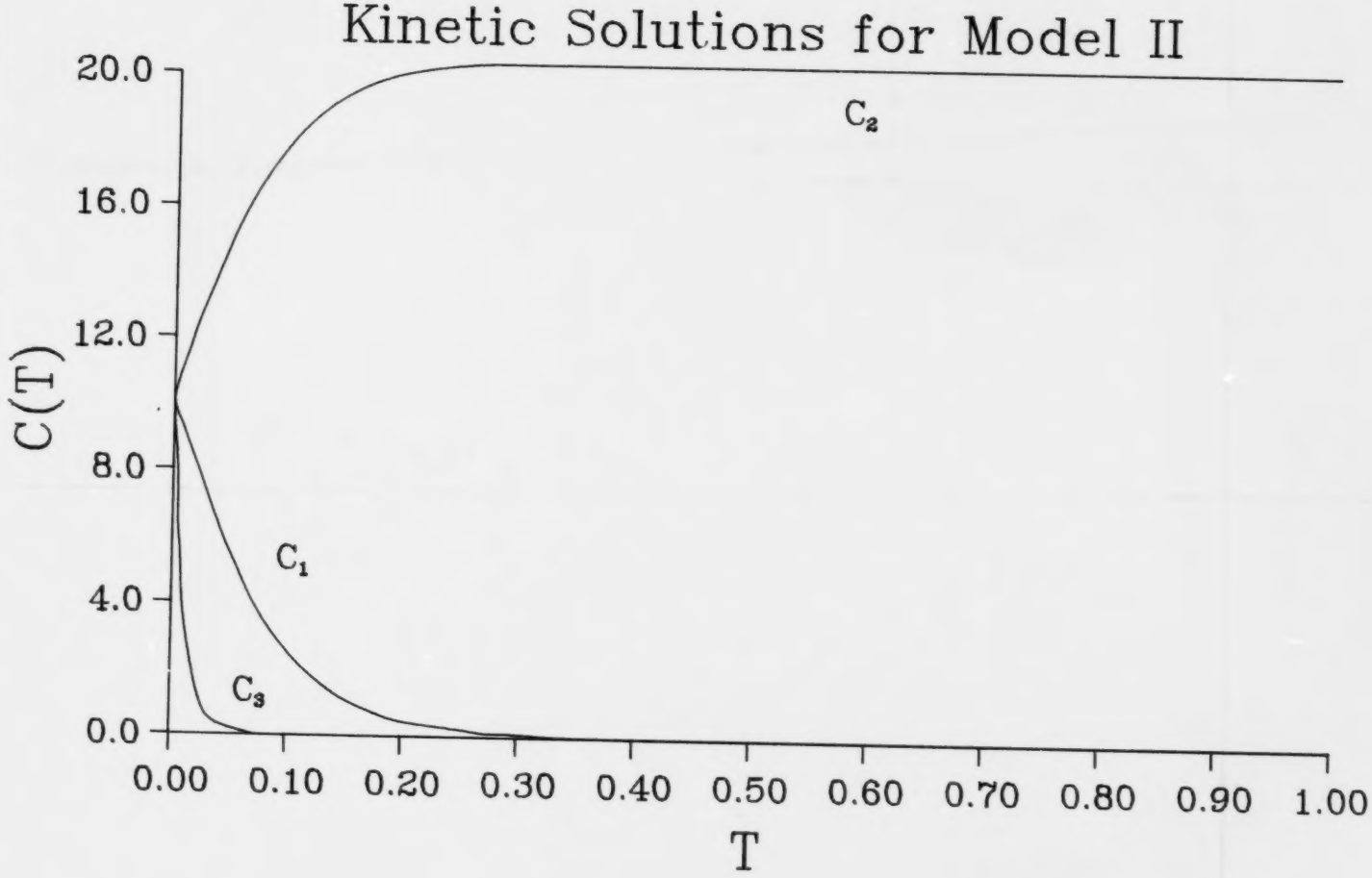

Figure 2 Dimensionless Concentrations vs Dimensionless Time $C_i(0)=10$

Secondly, writing $\varepsilon = k_1 K/k_3$,

$$\frac{1}{\varepsilon C_1}\ \frac{dC_1}{dt} = -C_2 = \frac{1 + C_3}{C_3}\ \frac{dC_3}{dt}$$

which upon integration yields

$$C_1 = E_2 C_3^{\varepsilon} \exp[\varepsilon\ C_3]. \tag{40}$$

The final equation for C_3 comes from substituting (39) into the last two terms of (38), that is

$$\frac{dC_3}{dt} = -\frac{C_3}{1 + C_3}\ [E_1 - C_3]. \tag{41}$$

The integral of (41), by classical methods, is

$$C_3^{1/E_1}\ (E_1 - C_3)^{-(1 + \frac{1}{E_1})} = E_3 e^{-t} \tag{42}$$

where $E_1 = C_2(0) + C_3(0) > 0$, $E_1 > C_3(t)$ for all t and E_3 is a positive constant.

Equation (42) suggests the possibility of multiple solutions and indeed they do exist as one can easily see for the case when $E_1 = 1$. But only one of these is less than or equal to E_1 and only that one remains thusly as $t \to \infty$.

Remark 6: We go no further with this analysis here since the model is of questionable utility. The reason for this question lies in equation (40) where it is seen that as $C_3 \to 0$ so does $C_1 \to 0$. However, we shall see equation (42) again in Model IV where a detailed analysis will be presented.

Model IV

This fourth model replaces the first equation of (37) with

$$\frac{d\hat{C}_1}{dt} = -k_1\hat{C}_1\hat{C}_2\hat{C}_3$$

but retains the last two equations which reflect Monod kinetics. With

$t = k_2\tau$, $C_1 = \hat{C}_1/\hat{C}_1(0)$, $C_2 = k_3\hat{C}_2/k_2K$ and $C_3 = \hat{C}_3/K$

the dimensionless equations become

$$\frac{dC_1}{dt} = -\frac{k_1K^2}{k_3}C_1C_2C_3, \quad \frac{dC_2}{dt} = \frac{C_2C_3}{1+C_3} = -\frac{dC_3}{dt} \tag{43}$$

As in Model III

$$C_2(t) = E_1 - C_3(t)$$

while

$$C_1(t) = E_2 \exp\left[\frac{k_1K^2}{k_3}(C_3 + C_3^2/2)\right]. \tag{44}$$

Equation (44) is quite different from the corresponding result for C_1 in Model III (compare (40)). Clearly, as $C_3 \to 0$, $C_1 \to E_2$, a reasonable situation.

Now the solution of the preceding Model (III) holds for C_3, that is equation (42) is valid. Since nonuniqueness was alluded to in the analysis of Model III we show that is not true now for $0 \le C_3 \le E_1$, that is in the proper physical range. However, there are other solutions outside this range in general.

To study the general case we rewrite (42) as

$$C_3^{1/E_1} = E_3 e^{-t}(E_1 - C_3)^{(1 + 1/E_1)} \qquad (45)$$

and remark that E_1, E_3 and C_3 are positive, and the interval of interest for C_3 is $0 \le C_3 \le E_1$. The left hand side is monotone increasing from 0 to $(E_1)^{1/E_1}$ on this range since the derivative is positive there. Similarly the right hand side is monotone decreasing from $E_3 e^{-t}(E_1)^{1+(1/E_1)}$ to zero on that range since its derivative is always negative there. Thus there is only one solution, the so called fixed point, of (45) for each value of "time" t. This establishes that the solution is unique on this range.

4. DETERMINATION OF RATE CONSTANTS FOR MODEL I

From Section 3 the solution of the dimensioned kinetic equations $\hat{C}_1'(\tau) = -k_1\hat{C}_1\hat{C}_2$, $\hat{C}_2'(\tau) = k_2\hat{C}_2\hat{C}_3$, $\hat{C}_3'(\tau) = -k_3\hat{C}_2\hat{C}_3$ is

$$\hat{C}_1(\tau)/\hat{C}_1(0) = [\hat{C}_3(\tau)/\hat{C}_3(0)],^{k_1/k_3} \tag{46}$$

$$\hat{C}_2(\tau) - \hat{C}_2(0) = (k_2/k_3)[\hat{C}_3(0) - C_3(\tau)] \tag{47}$$

and

$$\hat{C}_3(\tau) = E_2/[E_2E_4 \exp(E_2k_3\tau) + k_2/k_3], \tag{48}$$

where $E_2 = \hat{C}_2(0) + k_2\hat{C}_3(0)/k_3$ and $E_4 = 1/\hat{C}_3(0) - k_2/k_3E_2$.

By taking logarithms the ratio k_1/k_3 is obtained from (46) as

$$k_1/k_3 = \ln[\hat{C}_1(\tau)/\hat{C}_1(0)]/\ln[\hat{C}_3(\tau)/\hat{C}_3(0)], \tau > 0 \tag{49}$$

If Model I is correct the ratio should be sensibly constant. In practice there will be errors in the data. Thus more than one sample should be used. The chemical process should be sampled at n times, τ_j, $j = 1,\cdots,n$ for values of $\hat{C}_1(\tau_j)$, $\hat{C}_2(\tau_j)$ and $\hat{C}_3(\tau_j)$. At each sample point calculate the ratio k_1/k_3 by means of (49). Then calculate the mean of these values and use that value as the expected value of k_1/k_3 - that is

$$k_1/k_3 = \sum_1^n (k_1/k_3)_j/n$$

To obtain k_2/k_3 use (47) rewritten as

$$k_2/k_3 = [\hat{C}_2(\tau) - \hat{C}_2(0)]/[\hat{C}_3(0) - \hat{C}_3(\tau)]. \qquad (50)$$

Using the sample values take

$$k_2/k_3 = \sum_1^n (k_2/k_3)_j/n$$

where the $(k_2/k_3)_j$ are computed from measured values at τ_j which are substituted into (50).

Lastly, use

$$k_3 = (E_2\tau)^{-1}\ln\{[E_2/\hat{C}_3(\tau) - k_2/k_3]/E_2E_4\}, \ \tau > 0 \qquad (51)$$

to obtain k_3 by the sample and averaging process.

The algorithm for computing these ratios would be as follows:

(1) Sample $\hat{C}_1$, $\hat{C}_2$, and $\hat{C}_3$ at n points τ_j, j=1,2,$\cdots$,n with $\tau_j > 0$.

(2) Compute k_1/k_3 from (49) and use the averaging process described above.

(3) Compute k_2/k_3 from (50) and use the averaging process.

(4) Compute $E_2 = \hat{C}_2(0) + k_2\hat{C}_3(0)/k_3$.

(5) Compute $E_4 = [\hat{C}_3(0)]^{-1} - k_2/k_3E_2$.

(6) Compute k_3 from (51) and the averaging process.

(7) Compute the solutions $\hat{C}_1(\tau)$, $\hat{C}_2(\tau)$ and $\hat{C}_3(\tau)$ from (46), (47) and (48), respectively, as continuous functions of time, τ, using the values of the ratios obtained previously.

(8) The individual rate constants can be computed from points (6), (2) and (3).

5. EXACT PLUG FLOW SOLUTIONS

In this section we generalize the kinetic equations to include the effects of transport -- that is the equations will be the first order partial differential equations

$$\frac{\partial \hat{C}_1}{\partial \tau} + \bar{v} \frac{\partial \hat{C}_1}{\partial \bar{x}} = -k_1 f_1(\hat{C}_1, \hat{C}_2, \hat{C}_3)$$

$$\frac{\partial \hat{C}_2}{\partial \tau} + \bar{v} \frac{\partial \hat{C}_2}{\partial \bar{x}} = k_2 f_2(\hat{C}_1, \hat{C}_2, \hat{C}_3)$$

$$\frac{\partial \hat{C}_3}{\partial \tau} + \bar{v} \frac{\partial \hat{C}_3}{\partial \bar{x}} = -k_3 f_3(\hat{C}_1, \hat{C}_2, \hat{C}_3)$$

with the same choices of f_1, f_2, and f_3 as were presented in Section 3. Further, no additional dimensional analysis is necessary. Two approaches to obtain the exact solutions will be demonstrated in detail for Model I only. The amount of detail will be reduced for the other models.

Model I

From equations (11), (12), and (13), with all $D_i \equiv 0$, the model equations are

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = -C_1 C_2 \qquad (52a)$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = C_2 C_3 \qquad (52b)$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = -RC_2C_3 \ , \quad R = k_3/k_1 \tag{52c}$$

First Method: In this first method we introduce a convected coordinate

$$\eta = x + t \tag{53}$$

whereupon equations (52) transform to

$$\frac{dC_1}{d\eta} = -\frac{1}{2} C_1C_2, \ \frac{dC_2}{d\eta} = \frac{1}{2} C_2C_3, \ \frac{dC_3}{d\eta} = -\frac{R}{2} C_2C_3 \ :$$

Except for the scale factor of 1/2 these are the same as equations (26), (27) and (28). Their solution is

$$C_3 = \frac{2E_2}{E_2E_4 \exp[E_2R(x + t)] + 1/R}$$

$$C_1 = E_1(\frac{1}{2} C_3)^{1/R} \tag{54}$$

$$C_2 = 2E_2 - \frac{1}{R} C_3$$

where we have retained the same constants as used in Model I of Section 3.

With this method there are only arbitrary constants E_1, E_2 and E_4 whereas the second method permits arbitrary functions thereby expanding the domain of permissible problems.

Second Method: Here equations (52) will be solved directly using the method of characteristics (see e.g. Ames [10]). From (52b and c) it is clear that

$$\frac{\partial}{\partial t}\left(C_2 + \frac{1}{R} C_3\right) + \frac{\partial}{\partial x}\left(C_2 + \frac{1}{R} C_3\right) = 0 \qquad (55)$$

The Lagrange equations for this equation are

$$\frac{dt}{1} = \frac{dx}{1} = \frac{d\left(C_2 + \frac{1}{R} C_3\right)}{0}$$

with characteristics $\omega = x - t$ and $C_2 + \frac{1}{R} C_3$ constant along that characteristic. Thus

$$C_2(x,t) + \frac{1}{R} C_3(x,t) = F(x-t) \qquad (56)$$

where F is an arbitrary function.* (Already we see a difference in the two methods.)

Rewriting (52a and c) we find

$$\frac{\partial}{\partial t}\left(\ln C_1 - \frac{1}{R} \ln C_3\right) + \frac{\partial}{\partial x}\left(\ln C_1 - \frac{1}{R} \ln C_3\right) = 0$$

so that

$$\frac{C_1}{C_3^{1/R}} = G(x-t) \qquad (57)$$

where G is arbitrary. Finally, setting (56) into (52c) and integrating we have

$$C_3(x,t) = \frac{R\, F(x-t)}{1 + H(x-t)\, \exp[Rt\, F(x-t)]} \qquad (58)$$

where H is another arbitrary function. Clearly (58) is much more general than the first result of (54).

*According to the theory the most general solution of (49) is $F\left(C_2 + \frac{1}{R} C_3,\ x-t\right) = 0$ where F is arbitrary.

To evaluate the arbitrary functions, F, G, and H we need only specify

<u>initial data</u> $C_1(x,0) = f(x)$, $C_2(x,0) = g(x)$ and $C_3(x,0) = h(x)$ or

<u>boundary data</u> $C_1(0,t) = j(t)$, $C_2(0,t) = k(t)$ and $C_3(0,t) = m(t)$.

We illustrate the method of determining F, G, and H using the initial data. Using (50) it is clear that

$$C_2(x,0) + \frac{1}{R} C_3(x,0) = F(x) .$$

Hence $F(x) = g(x) + \frac{1}{R} h(x)$ which determines the function's form. In a similar way, from (57),

$$G(x) = f(x)/[h(x)]^{1/R}$$

and

$$H(x) = Rg(x)/h(x).$$

Finally, we can rewrite (56), (57), and (58) as

$$C_2(x,t) = g(x-t) + \frac{1}{R} h(x-t) - \frac{1}{R} C_3(x,t)$$

$$C_1(x,t) = f(x-t)[C_3(x,t)/h(x-t)]^{1/R}$$

and

$$C_3(x,t) = \frac{h(x-t)[Rg(x-t) + h(x-t)]}{h(x-t) + Rg(x-t)\ \exp\{t[Rg(x-t) + h(x-t)]\}}$$

In an analogous way one can employ the boundary data to determine the arbitrary functions.

Model II

For this model the equations become (see (14, 15, 16))

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = -C_1C_2C_3 \tag{59a}$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = C_2C_3 \tag{59b}$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = -SC_2C_3 \tag{59c}$$

where $S = k_3k_2L/k_1\bar{v}$. Since (59b) and (59c) are similar to (52b) and (52c), with S replacing R, it follows that

$$C_2(x,t) + \frac{1}{S} C_3(x,t) = F(x-t)$$

and

$$C_3(x,t) = \frac{SF(x-t)}{1 + H(x-t)\ \exp[StF(x-t)]} .$$

However, (59a) is quite different from (52a). To study its relation to C_3 divide by C_1 and subtract (59c) divided by S to obtain

$$\frac{\partial}{\partial t}[\ln C_1 - \frac{1}{S} C_3] + \frac{\partial}{\partial x}[\ln C_1 - \frac{1}{S} C_3] = 0 .$$

The solution of this equation is

$$C_1(x,t) = G(x-t)e^{C_3(x,t)/S}$$

where G is the third arbitrary function.

As in Model I the arbitrary functions are uniquely determinable from boundary or initial data (loading of the stream).

Model III

In this case we draw our equations from (17, 18 and 19) as

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = -C_1 C_2 \tag{60a}$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \alpha \frac{C_2 C_3}{1 + C_3} \tag{60b}$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = -\beta \frac{C_2 C_3}{1 + C_3} \tag{60c}$$

where $\alpha = k_2 L/\bar{v}$ and $\beta = k_3/Kk_1$.

The relationship

$$\frac{1}{\alpha} C_2(x,t) + \frac{1}{\beta} C_3(x,t) = F(x-t) \tag{61}$$

follows immediately from (60b) and (60c). From (60a) we have

$$\frac{\partial \ln C_1}{\partial t} + \frac{\partial \ln C_1}{\partial x} = -C_2$$

and from (60c)

$$\frac{\partial}{\partial t}\left[\frac{1}{\beta}(\ln C_3 + C_3)\right] + \frac{\partial}{\partial x}\left[\frac{1}{\beta}(\ln C_3 + C_3)\right] = -C_2$$

Consequently, by already familiar processes,

$$C_1(x,t) = G(x-t)\, C_3^{1/\beta} \exp[C_3/\beta]$$

is the relationship between C_1 and C_3.

Last, we must solve for $C_3(x,t)$ the equation obtained from (60c) by substituting (61) when solved for C_2. This will be done

in Model IV since the analysis is exactly the same and Model IV is more reasonable (compare Section 3, Model IV).

Model IV

Here our equations are taken from (20), (21) and (22) of Section 2 with all $D_i \equiv 0$, that is

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} = - C_1 C_2 C_3 \tag{62a}$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} = \alpha \frac{C_2 C_3}{1 + C_3} \tag{62b}$$

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = - \gamma \frac{C_2 C_3}{1 + C_3} \tag{62c}$$

where $\gamma = k_3/K^2 k_1$, and $\alpha = k_2 L/\bar{v}$.

Because of the similarity between (62b,c) and (60b,c) it follows that

$$\frac{1}{\alpha} C_2(x,t) + \frac{1}{\gamma} C_3(x,t) = F(x-t). \tag{63}$$

From (62a) we have

$$\frac{\partial \ln C_1}{\partial t} + \frac{\partial \ln C_1}{\partial x} = -C_2 C_3$$

and also

$$\frac{\partial}{\partial t} \left[\frac{1}{\gamma} \left(C_3 + \frac{C_3^2}{2}\right)\right] + \frac{\partial}{\partial x} \left[\frac{1}{\gamma} \left(C_3 + \frac{C_3^2}{2}\right)\right] = -C_2 C_3$$

Consequently, (compare (44)),

$$C_1(x,t) = G(x,t) \exp\left[\frac{1}{\gamma} \left(C_3 + C_3^2/2\right)\right]$$

provides the relation between C_1 and C_3. Finally, the equation for C_3 is the nonlinear equation

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_3}{\partial x} = -\gamma\alpha \frac{C_3}{1 + C_3}\left[F(x-t) - \frac{1}{\gamma} C_3\right] \tag{64}$$

which integrates in a manner similar to (41), except we use characteristics. The result is

$$C_3(F - \frac{1}{\gamma} C_3)^{-(\gamma F+1)} = e^{-\gamma\alpha t F} H(x-t),$$

or the more easily computable form

$$\ln C_3 - (1 + \gamma F) \ln(F - \frac{1}{\gamma} C_3) = -\alpha\gamma t F + K(x-t).$$

Here, $K = \ln H$ is an arbitrary function and F is the arbitrary function of equation (63).

Remark 7: The flow velocity in rivers is rarely constant. Here we shall describe the determination of analytic solutions for Model I in the case where after dimensional analysis the equations* are (see (52))

$$\frac{\partial C_1}{\partial t} + u\,(x) \frac{\partial C_1}{\partial x} = -C_1 C_2 \tag{65a}$$

$$\frac{\partial C_2}{\partial t} + u\,(x) \frac{\partial C_2}{\partial x} = C_2 C_3 \tag{65b}$$

$$\frac{\partial C_3}{\partial t} + u\,(x) \frac{\partial C_3}{\partial x} = -R C_2 C_3 \tag{65c}$$

As in the development of equation (55),

$$\frac{\partial}{\partial t}\,(C_2 + \frac{1}{R} C_3) + u\,(x) \frac{\partial}{\partial x}\,(C_2 + \frac{1}{R} C_3) = 0 \tag{66}$$

*Assuming no lateral inflow.

The Lagrange system for this equation is

$$\frac{dt}{1} = \frac{dx}{u(x)} = \frac{d(C_2 + \frac{1}{R} C_3)}{0} .$$

With

$$U(x) = \int^{x} \frac{d\eta}{u(\eta)}$$

the solution* of (66) is

$$C_2 + \frac{1}{R} C_3 = F[U(x)-t] \tag{67}$$

From (65a) and (65c) it follows that

$$C_1/C_3^{1/R} = G[U(x) - t] \tag{68}$$

Finally, using (67) in (65c) the equation for C_3 becomes

$$\frac{\partial C_3}{\partial t} + u(x) \frac{\partial C_3}{\partial x} = -R C_3 F + C_3^2$$

Integration of this equation gives

$$C_3(x,t) = \frac{R F[U(x)-t]}{1 + H[U(x) - t]\exp\{R t F[U(x) - t]\}}$$

All other cases can be carried out in the same way with the characteristic

$$U(x) - t = \text{constant}$$

as the natural generalization of x-t = constant.

*Of course, if $u(x) = 1$, $U(x) = x$ as in the Model discussions.

6. SOME RESULTS ON THE FULL SYSTEM

In this section we present some preliminary analytic results for the full systems including diffusion effects. The equations are those of Section 2 (Models I-IV). A number of possibilities will be explored including traveling wave and invariant solutions.

6.1. Relationship between $\hat{C}_2$ and $\hat{C}_3$ for all Models.

In the interesting case where $D_2 = D_3$ and* $f_2(\hat{C}_2,\hat{C}_3) \equiv f_3(\hat{C}_2,\hat{C}_3)$ in equations (1), (2), and (3) a relationship always exists between $\hat{C}_2$ and $\hat{C}_3$. To obtain it we divide (2) by k_2 and (3) by k_3 and add the two equations whereupon

$$\frac{\partial}{\partial\tau}\left[\frac{1}{k_2}\hat{C}_2 + \frac{1}{k_3}\hat{C}_3\right] + \bar{v}\frac{\partial}{\partial\bar{x}}\left[\frac{1}{k_2}\hat{C}_2 + \frac{1}{k_3}\hat{C}_3\right] = D_2\frac{\partial^2}{\partial\bar{x}^2}\left[\frac{1}{k_2}\hat{C}_2 + \frac{1}{k_3}\hat{C}_3\right]$$

-- a linear diffusion equation. This can be solved by classical methods using the boundary and initial data for $\frac{1}{k_2}\hat{C}_2 + \frac{1}{k_3}\hat{C}_3$.

Calling that solution $F(\bar{x},\tau)$ -- i.e.

*This last assumption, i.e. $f_2 \equiv f_3$ is true for all models.

$$\frac{1}{k_2}\hat{C}_2 + \frac{1}{k_3}\hat{C}_3 = F(\bar{x},\tau)$$

it follows that $\hat{C}_3$ satisfies the equation

$$\frac{\partial \hat{C}_3}{\partial \tau} + \bar{v}\ \frac{\partial \hat{C}_3}{\partial \bar{x}} = D_2\ \frac{\partial^2 \hat{C}_3}{\partial \bar{x}^2} - k_3 f_3\left[k_2\ F(\bar{x},\tau) - \frac{k_2}{k_3}\hat{C}_3, \hat{C}_3\right]$$

For Model I the last term in the right hand side would be

$$-k_3 k_2\ F(\bar{x},\tau)\ \hat{C}_3 + k_2 \hat{C}_3^{\,2}$$

and for Model IV it would be

$$\frac{-k_3 k_2\ F\hat{C}_3 + k_2 \hat{C}_3^{\,2}}{K + \hat{C}_3}$$

6.2 Traveling Wave Solutions

For all of the full systems we can search for solutions of the form

$$C_i(x,t) = C_i(x-t) = C_i(\eta) \qquad (69)$$

which represent concentration waves travelling to the right (downstream) with velocity 1. All models will support such travelling wave solutions. Here we discuss it for Model II (see equations (14), (15) and (16)). From (69) it follows immediately that $\frac{\partial C_i}{\partial x} = \frac{dC_i}{d\eta}$ and $\frac{\partial C_i}{\partial t} = -\frac{dC_i}{d\eta}$ whereupon equations (14), (15), and (16) become

$$\frac{d^2 C_1}{d\eta^2} = N_{Pe}^{(1)} C_1 C_2 C_3 \qquad (70a)$$

$$\frac{d^2C_2}{d\eta^2} = -N_{Pe}^{(2)} C_2C_3 \qquad (70b)$$

$$\frac{dC_3}{d\eta^2} = N_{Pe}^{(3)} \frac{k_3k_2L}{k_1\bar{v}} C_2C_3 = \gamma C_2C_3 \qquad (70c)$$

which are ordinary differential equations. Explicit exact solutions are possible for this system under certain conditions. From (70b) and (70c) it always follows that

$$C_2(\eta) + \frac{N_{Pe}^{(2)}}{\gamma} C_3 = \lambda_1\eta + \lambda_2,$$

where λ_1 and λ_2 are arbitrary constants. The equation for C_3 becomes

$$\frac{d^2C_3}{d\eta^2} = \gamma C_3(\lambda_1\eta + \lambda_2 - \frac{N_{Pe}^{(2)}}{\gamma} C_3). \qquad (71)$$

Equation (71) is autonomous if $\lambda_1 = 0$. The integration is then accomplished by setting $p_3 = \frac{dC_3}{d\eta}$ from which it follows that

$\frac{d^2C_3}{d\eta^2} = p_3 \frac{dp_3}{dC_3}$. Then (71) integrates to

$$p_3^2 = \lambda_2\gamma C_3^2 - 2 \frac{N_{Pe}^{(2)}}{3} C_3^3 + \lambda_3$$

and a second integration gives rise to elliptic functions (with $\lambda_3 \neq 0$) and a logarithmic form (with $\lambda_3 = 0$).

For Model IV the ordinary differential eautions for a traveling wave solution are

$$\frac{d^2C_1}{d\eta^2} = N_{Pe}^{(1)} C_1C_2C_3$$

$$\frac{d^2C_2}{d\eta^2} = -N_{Pe}^{(2)} \frac{k_2L}{\bar{v}} \frac{C_2C_3}{1 + C_3}$$

$$\frac{d^2C_3}{d\eta^2} = N_{Pe}^{(3)} \frac{k_3}{K^2 k_1} \frac{C_2 C_3}{1 + C_3}$$

with $\eta = x - t$, as before.

Remark 8: All models possess travelling wave solutions. For Models I and II these will be constructed in the next section.

6.3 Invariant (Similar) Solutions

The general group theory and techniques for constructing these solutions is given in Ames [10,11]. While these equations, for all models, are invariant under time and space translations they are not invariant under the dilatation or spiral groups. Thus there are no similar solutions for any of these models.

7. TRAVELLING WAVE SOLUTIONS FOR MODELS I AND II

The remarks of Section 6II are amplified here by explicitly calculating a travelling wave solution for Models I and II. The solutions for C_2 and C_3 are calculated exactly and that for C_1 by a perturbation analysis. With $\beta = N_{Pe}^{(1)} = N_{Pe}^{(2)} = N_{Pe}^{(3)}$ and $\lambda = \frac{k_3}{k_1}$ for Model I, and $\lambda = \frac{k_3 k_2 L}{k_1 \bar{v}}$ for Model II, we use (11-13) for Model I and (14-16) for Model II. Except for the different values of λ equations (12,13) and (15,16) are the same!

Using $C_1 = f(\eta)$, $C_2 = g(\eta)$, $C_3 = h(\eta)$, $\eta = x-t$, the two systems become

$$\frac{d^2 f}{d\eta^2} = \beta f g, \quad \frac{d^2 g}{d\eta^2} = -\beta g h, \quad \frac{d^2 h}{d\eta^2} = \lambda \beta g h \tag{72}$$

for Model I, and

$$\frac{d^2 f}{d\eta^2} = \beta f g h, \quad \frac{d^2 g}{d\eta^2} = -\beta g h, \quad \frac{d^2 h}{d\eta^2} = \lambda \beta g h \tag{73}$$

for Model II. From the last two, we deduce the conservation law

$$\frac{1}{\lambda} h(\eta) + g(\eta) = E(\text{constant}) \tag{74}$$

where we have discarded linear growth (or decay) with η.

Using (74) in the equation for h (either (72) or (73)) results in the nonlinear equation.

$$\frac{d^2h}{d\eta^2} = E\beta\lambda h - \beta h^2. \tag{75}$$

The transformation $\omega^2 = E\beta\lambda\eta^2$ changes (75) into

$$\frac{d^2h}{d\omega^2} = h - \frac{h^2}{E\lambda} \tag{75a}$$

When (75a) is multiplied by $2\frac{dh}{d\omega}$ and integrated with respect to ω, in the interval 0 to ω, there results

$$(\frac{dh}{d\omega})^2 = h^2 - \frac{2}{3E\lambda} h^3 + [\frac{dh(0)}{d\omega}]^2 - [h^2(0) - \frac{2}{3E\lambda} h^3(0)], \tag{76}$$

where $h(0)$ and $\frac{dh(0)}{d\omega}$ are initial values of h and $\frac{dh}{d\omega}$. Because of physical reasons, $\lim_{\omega\to\infty} h(\omega) = \lim_{\omega\to\infty} \frac{dh}{d\omega} = 0$ which can only be true in (76) if

$$[\frac{dh(0)}{d\omega}]^2 - [h^2(0) - \frac{2}{3E\lambda} h^3(0)] = 0.$$

From the two possible signs for $\frac{dh}{d\omega}$ in (76) we choose the negative one, on physical grounds, which yields

$$\frac{dh}{d\omega} = -h(1+ah)^{1/2}, \quad a = -\frac{2}{3E\lambda} \tag{77}$$

where $0 \leq h \leq \frac{3}{2} E\lambda$ is required. For $h > \frac{3}{2} E\lambda$ equation (76) cannot have real solutions and $h < 0$ is of no physical interest.

With the initial condition $h(0) = \theta$, $0 < \theta < \frac{3}{2} E\lambda$, equation (77) integrates to

$$h(\omega) = \frac{\theta}{[\cosh \frac{\omega}{2} + (1 - \frac{2\theta}{3E\lambda})^{1/2} \sinh \frac{\omega}{2}]^2}$$

or in the original coordinates

$$h(\bar{x}-\bar{t}) = \frac{\theta}{\left[\cosh\left(\sqrt{E\beta\lambda}\,\frac{\bar{x}-\bar{t}}{2}\right) + \left(1 - \frac{2\theta}{3E\lambda}\right)^{1/2} \sinh\left(\sqrt{E\beta\lambda}\,\frac{\bar{x}-\bar{t}}{2}\right)\right]^2}. \tag{78}$$

and, from (74) we have

$$g(\omega) = E - \frac{\theta}{\lambda}\left[\cosh\frac{\omega}{2} + \left(1 - \frac{2}{3E\lambda}\right)^{1/2} \sinh\frac{\omega}{2}\right]^{-2} \tag{79}$$

Remark 9: Equation (76), with the constant term equal to zero and with the boundary conditions $h(0) = \theta$, $\lim_{\omega\to\infty} h = 0$ has other solutions if we do not insist on the negative sign in (77). For example,

$$\tilde{h}(\omega) = \theta\left[\cosh\frac{\omega}{2} - (1 + a\theta)^{1/2}\sinh\frac{\omega}{2}\right]^{-2}$$

is also a solution satisfying the boundary conditions. This solution achieves a maximum of $\frac{3}{2}E\lambda$, for $\omega_0 > 0$, and then begins to decay. For this reason, it is not of physical interest.

Now, fixing on Model I, the equation for f (see (72)) becomes the linear equation

$$\frac{d^2f}{d\eta^2} - (\beta g)f = 0$$

with (79) for g. For Model II the equation for f (see (73)) becomes the linear equation

$$\frac{d^2f}{d\eta^2} - (\beta g h)f = 0$$

In both models the equation for f is linear, but has difficult variable coefficients. As an easily computed alternative, we develop a perturbation solution in the next Section, useful in computation with large λ. The validity of the perturbation solution is esta - blished by comparison with the exact solutions for h and g just obtained.

8. PERTURBATION SOLUTIONS FOR MODELS I AND II

While equation (75) can be integrated exactly, a perturbation analysis will be useful in providing a solution for f in terms of elementary functions. In what follows, we shall write $R^2 = E$ and carry out a perturbation in $1/\lambda$ ($\lambda = \frac{k_3}{k_1}$ for Model I and $\frac{k_3 k_2 L}{k_1 \bar{v}}$ for Model II).

Upon dividing by $\lambda\beta$ and writing $\omega^2 = \lambda\beta\eta^2$ equation (75) becomes

$$\frac{d^2h}{d\omega^2} - R^2 h = -\frac{h^2}{\lambda} \quad , \tag{80}$$

subject to the (pulselike) condition $h(0) = \theta$ and $\lim_{\omega\to\infty} h = 0$.

A perturbation expansion in $1/\lambda$ is assumed to exist in the form

$$h = h_0 + (1/\lambda)h_1 + (1/\lambda)^2 h_2 + \cdots, \tag{81}$$

although we shall compute only the fist two terms. Upon substituting (81) into (80) and equating like powers of $1/\lambda$ the equations for h_0 and h_1 are

$$\frac{d^2h_0}{d\omega^2} - R^2 h_0 = 0, \; h_0(0) = \theta, \; h_0 \to 0 \text{ as } \omega\to\infty \; , \tag{82}$$

and

$$\frac{d^2h_1}{d\omega^2} - R^2 h_1 = -h_0^2, h_1(0)=0, h_1 \to 0 \text{ as } \omega\to\infty. \tag{83}$$

The solutions for (82) and (83) follow from standard elementary methods. They are

$$h(\omega) = \theta e^{-R\omega} + (1/\lambda)\theta^2(e^{-R\omega} - e^{-2R\omega})/3R^2,$$

or

$$h(x-t) = \theta \exp[-\sqrt{(k_3 N_{Pe} E/k_1)}\ (x-t)] + [(1/\lambda)\theta^2/3E]\{\exp[-\sqrt{(k_3 N_{Pe} E/k_1)}\ (x-t)] - \exp[-2\sqrt{(k_3 N_{Pe} E/k_1)}\ (x-t)]\}. \quad (84)$$

Next, g is obtained from the conservation law, (74), as

$$g(x-t) = E - (1/\lambda)\ h(x-t) \quad (85)$$

and f is obtained from $d^2f/d\eta^2 = \beta fg$ as follows. With $\phi^2 = \beta\eta^2$ this equation becomes

$$\frac{d^2f}{d\phi^2} - R^2 f = -(1/\lambda) fh. \quad (86)$$

Using $f = f_0 + (1/\lambda)f_1 + \cdots$, $h = h_0 + (1/\lambda)h_1 + \cdots$ and equating like powers of $1/\lambda$ the equations for f_0 and f_1 become

$$\frac{d^2f_0}{d\phi^2} - R^2 f_0 = 0$$

and

$$\frac{d^2f_1}{d\phi^2} - R^2 f_1 = -h_0 f_0.$$

The solution of these equations yields

$$f = Ke^{-R\phi} + (1/\lambda)K\theta[e^{-R\phi} - e^{-(1+\sqrt{\lambda})R\phi}]/R^2(\lambda + 2\sqrt{\lambda}), \quad (87)$$

where $f(0) = K$. The reader is also reminded that $\lambda = k_3/k_1$, $N_{Pe} = L\bar{v}/D$ and $\eta = x-t = (\bar{x} - \bar{v}\tau)/L$.

Equations (84), (85) and (87) provide a perturbation solution for h, g and f in the parameter $1/\lambda$. They display analytically how the Peclet Number, initial states and rate constant ratios affect the solution. In this unidirectional travelling wave solution x must always be larger than t and as $x-t \to \infty$, $C_1 = f(x-t) \to 0$, $C_2 = g(x-t) \to E_2$ and $C_3 = h(x-t) \to 0$.

Exact and perturbed solutions for h and g are compared in Figure 3 and 4 for a range of parameter values. They are indistinguishable for these ranges. Figure 5 shows the corresponding perturbed results for f.

For Model II, equations (84) and (85) provide the solution for h and g. To obtain that for f return to the first equation of (73) which becomes

$$\frac{d^2f}{d\phi^2} = (R^2 - \frac{1}{\lambda} h)hf \tag{88}$$

using (85) and $\phi^2 = \beta\eta^2$. With (81) for h equation (88) becomes

$$\frac{d^2f}{d\omega^2} - R^2h_0f = \frac{1}{\lambda} (Eh_1 - h_0^2)f + \cdots \tag{89}$$

Taking $f = f_0 + (1/\lambda)\ f_1 + \cdots$ and equating like powers of $1/\lambda$ the equations for f_0 and f_1 become

$$\frac{d^2f_0}{d\phi^2} - R^2h_0f_0 = 0 \tag{90}$$

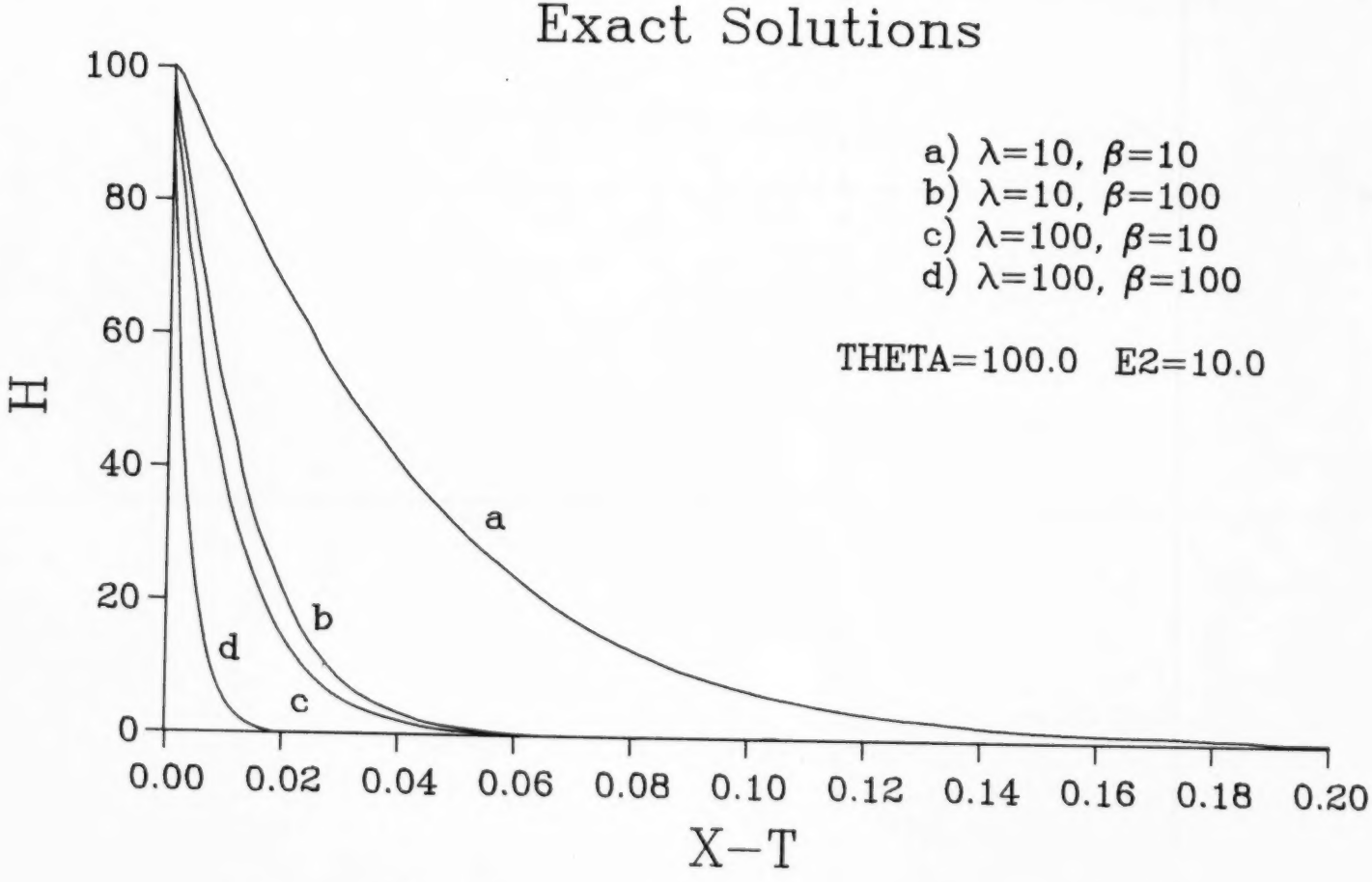

Figure 3 Exact Travelling Wave Solutions for H vs X−T.

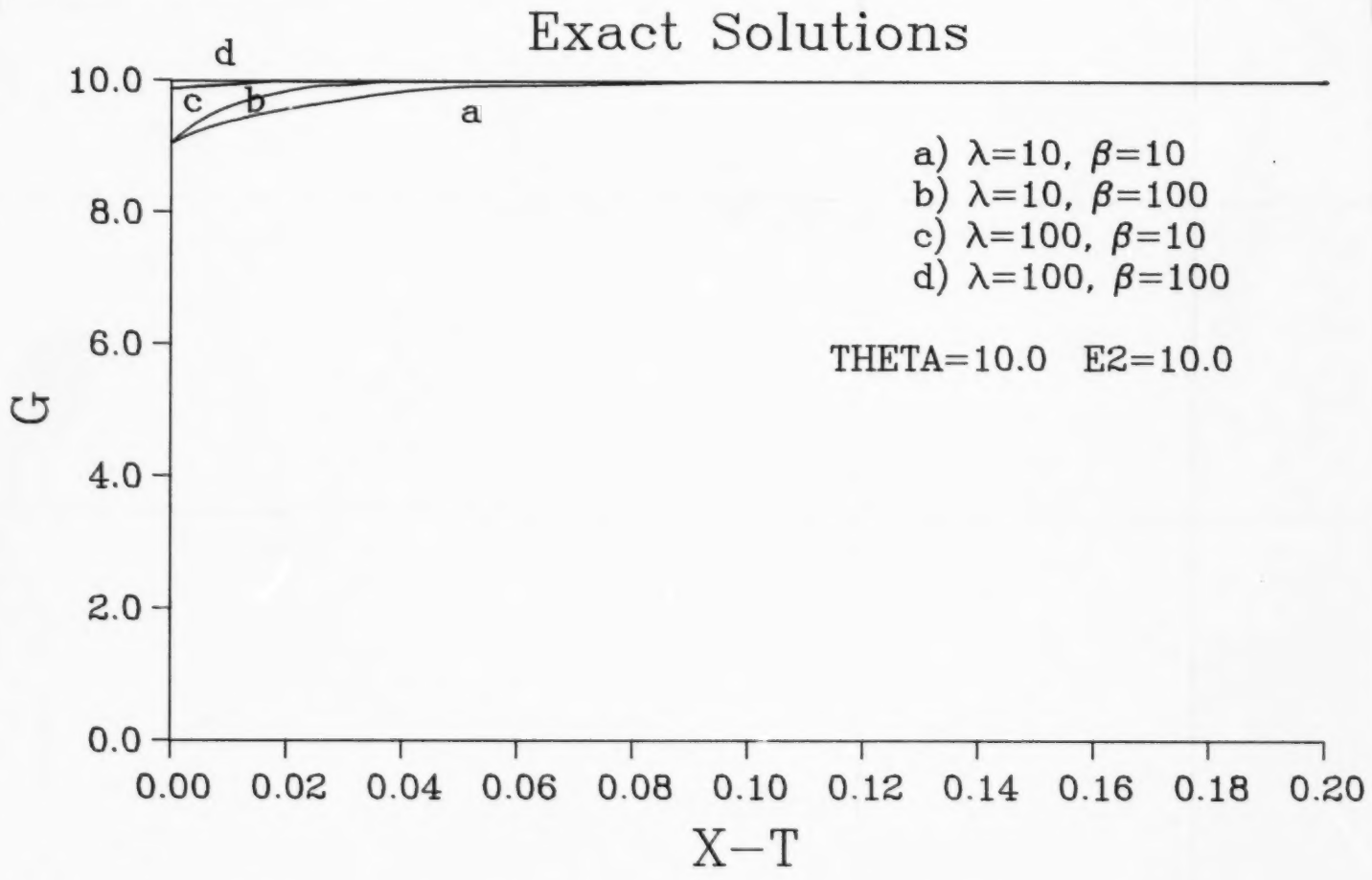

Figure 4 Exact Travelling Wave Solutions for G vs X−T.

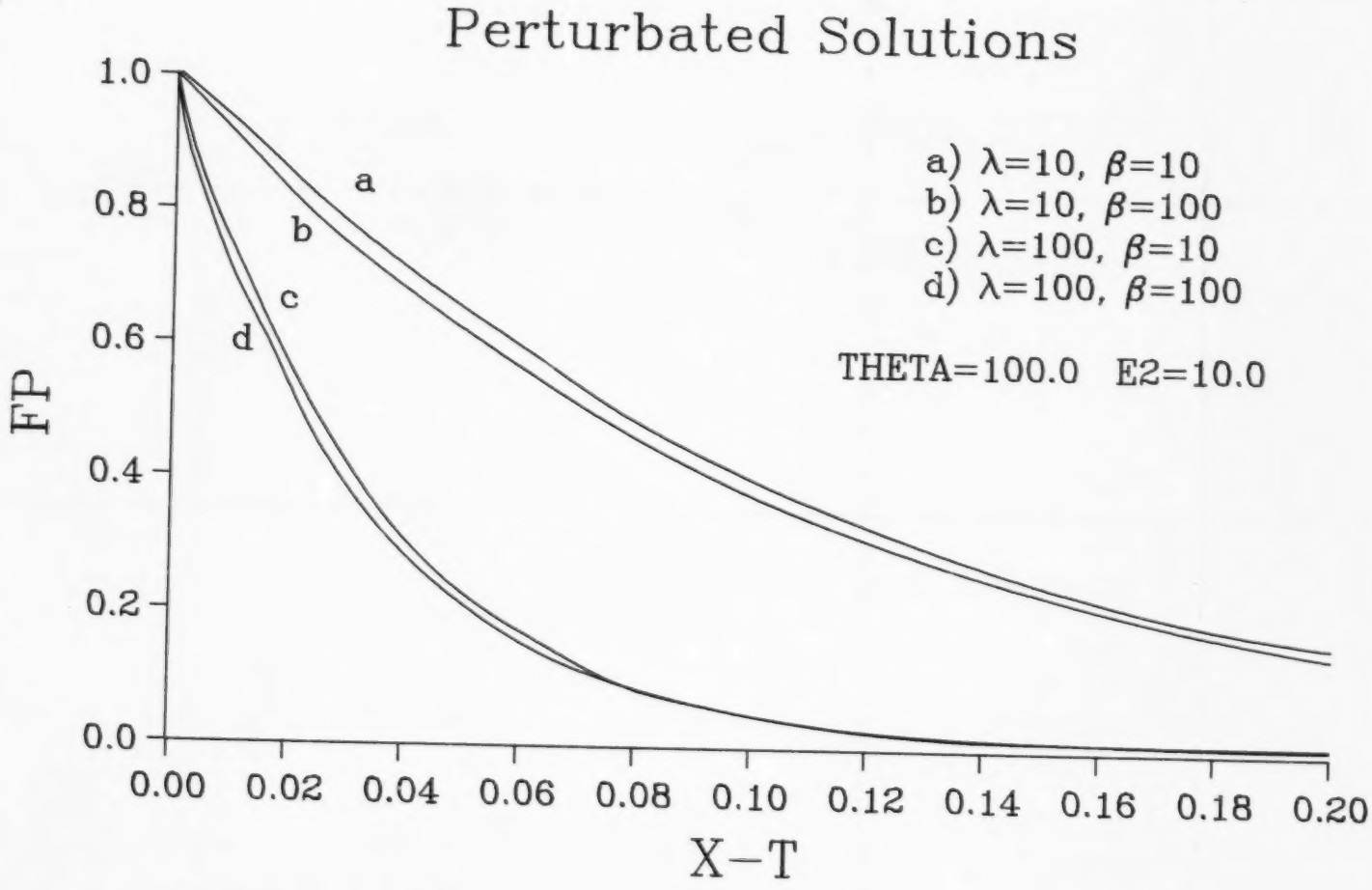

Figure 5 Perturbed Travelling Wave Solutions for F vs X−T.

and

$$\frac{d^2 f_1}{d\phi^2} - R^2 h_0 f_1 = (Eh_1 - h_0^2) f_0,$$

where h_0 and h_1 are the previously computed exponential functions ($h_0 = \theta \exp[-R\lambda\phi]$, $h_1 = \theta^2 (e^{-R\lambda\phi} - e^{-2R\lambda\phi})/3R^2$). Solutions of these equations involve Bessel functions and since they become quite complicated they will not be detailed here (see Kamke [12]). This complexity and the uncertainty about the values of the parameters in the problem suggests that simple bounds, which we develop later, will be more useful to the practitioner.

Perturbation solutions are also possible for the other models but their solution involves complex special functions which are more difficult to use.

9. UPPER AND LOWER BOUNDS FOR TRAVELLING WAVE SOLUTIONS

The complexities that appear, even in the perturbations of Model II, suggest that upper and lower bounds for the travelling wave solutions (and, later, the steady state solutions) will be of considerable use in analyzing these problems. These bounds, containing the parameters of the problem, are usually found by using the maximum (minimum) principle (see Protter and Weinberger [13] for example) or differential inequalities (see Walter [14] for example). Analytic bounds have numerous advantages over numerical solutions. They include:

a. a drastic reduction of computation time,

b. efficient parameter studies,

c. ease in studying limits ($t, x \to \infty$),

d. bounds are often handier to use than complicated exact solutions,

e. quality control of bounds trivially possible, while in numerics this is often not the case.

A typical result from Protter and Weinberger [13] is the following theorem.

Theorem. Suppose that $u(x)$ statisfies $u'' + h(x,u,u') = 0$ and the initial conditions $u(a) = \gamma_1$, $u'(a) = \gamma_2$. Suppose also that h, $\partial h/\partial u$ and $\partial h/\partial u'$ are continuous and $\partial h/\partial u \leq 0$. If $z_1(x)$ satisfies

$$z_1'' + h(x,z_1,z_1') \geq 0,$$

$$z_1(a) \geq \gamma_1, \; z_1'(a) \geq \gamma_2,$$

and if $z_2(x)$ satisfies

$$z_2'' + h(x,z_2,z_2') \leq 0,$$

$$z_2(a) \leq \gamma_1, \; z_2'(a) \leq \gamma_2,$$

then we have the upper and lower bounds

$$z_2(x) + \gamma_1 - z_2(a) \leq u(x) \leq z_1(x) + \gamma_1 - z_1(a)$$

$$z_2'(x) \leq u'(x) \leq z_1'(x).$$

We will utilize results such as this in our analysis.

9.1 Bounds for Travelling Wave Solutions of Pollutant Equation (f) for Models I and III

For both models I and III the pollutant, f, satisfies the equation

$$-\frac{d^2f}{d\eta^2} + \beta g(\eta) f(\eta) = 0 \qquad (91a)$$

with the boundary conditions

$$f(0) = f_0 > 0, \; \lim_{\eta \to \infty} \frac{df}{d\eta} = 0 \qquad (91b)$$

and the physical assumption

$$f(\eta) > 0 \text{ for all } \eta \geq 0 \tag{91c}$$

From the conservation laws

$$g = E - \frac{1}{\lambda} h \text{ (Model I)} \tag{92a}$$

$$g = E\lambda_2 - \lambda_2 h/\lambda_1 \text{ (Model III)} \tag{92b}$$

we have

$$\lim_{\eta\to\infty} g(\eta) = E \text{ for Model I,}$$

$$\lim_{\eta\to\infty} g(\eta) = E\lambda_2 \text{ for Model III,}$$

because of properties of the known solution for h.

Since $f > 0$ and $g > 0$ it is clear from (91a) that $f'' > 0$ and therefore f' is monotone increasing. But since $\lim_{\eta\to\infty} f' = 0$ it follows that $f' < 0$ and therefore f is monotone decreasing. Thus there exists a constant $c \geq 0$ such that $\lim_{\eta\to\infty} f(n) = c$. If we assume that $c > 0$ then $\lim_{\eta\to\infty} f'' = \lim_{\eta\to\infty} \beta g f = E\beta c > 0$ ($E\lambda_2\beta C$ for Model III) and therefore $\lim_{\eta\to\infty} f' = \infty$ in contradiction to (91b). Hence $c \equiv 0$ - i.e.

$$\lim_{\eta\to\infty} f(\eta) = 0 \tag{93}$$

Note: For an equation of the form, $-y'' + a(x)y = 0$ with boundary data $y(0) = 0$, $\lim_{x\to\infty} y(x) = 0$ there is a maximum and minimum principle whenever $a(x) > 0$ for all $x>0$. Thus if $-y'' + a(x)y \geq 0$ then $y \geq 0$ and if $-y'' + a(x)y \leq 0$ then $y \leq 0$. For details of this idea see Protter and Weinberger [13].

For Model I we introduce the comparison problem

$$-\bar{f}'' + \beta(E - \frac{\theta}{\lambda})\bar{f},\ \bar{f}(0) = f_0,\ \lim_{\eta\to\infty}\ \bar{f} = 0$$
$$-\underline{f}'' + E\beta\underline{f} = 0,\ \underline{f}(0) = f_0,\ \lim_{\eta\to\infty}\underline{f} = 0, \tag{94}$$

where $\theta = h(0)$. These problems have the solutions

$$\bar{f}(\eta) = f_0\ \exp\{-[\beta(E - \theta/\lambda)]^{1/2}\ \eta\}$$
$$\underline{f}(\eta) = f_0\ \exp\{-(E\beta)^{1/2}\eta\} \tag{95}$$

where the "upper bar" indicates the upper bound and the "lower bar" the lower bound.

For Model III consider the comparison problems

$$-\bar{f}'' + \beta\lambda_2(E - \frac{\theta}{\lambda_1})\bar{f} = 0,\ \bar{f}(0) = f_0,\ \lim_{\eta\to\infty}\bar{f}(\eta) = 0$$
$$-\underline{f}'' + E\beta\lambda_2\underline{f} = 0,\ \underline{f}(0) = f_0,\ \lim_{\eta\to\infty}\underline{f}(\eta) = 0 \tag{96}$$

whose solutions are

$$\bar{f} = f_0\ \exp\{-[\beta\lambda_2(E - \frac{\theta}{\lambda_1})]^{1/2}\eta\}$$
$$\underline{f} = f_0\ \exp\{-[E\beta\lambda_2]^{1/2}\eta\} \tag{97}$$

To verify that (96) are bounds for Model I we have for that model

$$0 = -f'' + \beta gf = -f'' + \beta(E - \frac{h}{\lambda})f \geq -f'' + \beta(E - \frac{\theta}{\lambda})f. \tag{98}$$

With $u = \bar{f} - f$, $u(0) = 0$, $\lim_{\eta\to\infty} u = 0$, the right hand side of equation (98), combined with the first equation of (94), gives

$$-u'' + \beta(E - \frac{\theta}{\lambda})u \geq 0 \tag{99}$$

The minimum principle (see the previous note) implies $u \geq 0$, that is $\bar{f}(\eta) \geq f(\eta)$ for $\eta \geq 0$.

In the same way we can show, using the maximum principle, that $\underline{f}(\eta) \leq f(\eta)$ for $\eta \geq 0$ and also that the solution for Model III has the upper and lower bounds as given by equation (97)

9.2 Bounds for Travelling Wave Solutions of Models II and IV

For Model IV the problem for the pollutant concentration f is

$$-f'' + \beta\lambda_2(E - \frac{1}{\lambda_1} h)hf = 0, \quad f(0) = f_0 > 0, \quad \lim_{\eta\to\infty} f' = 0, \tag{100}$$

Since $g/\lambda_2 + h/\lambda_1 = E$ and $0 < h(\eta) < E\lambda_1$ for all $\eta \geq 0$ it follows that $\lim_{\eta\to\infty} f(\eta) > 0$. Bounds on h can be determined using a phase plane analysis. When h is known, and hence g, this equation is linear but has complicated variable coefficients. Solutions of comparison problems, similar to (94) and (96), are expressible in terms of Bessel functions which, in turn, can be estimated as detailed below:

$$f_0\, e^{-a/m^2}(1 + \frac{a}{m^2} e^{-m\eta}) \leq \underline{f} \leq f \leq \bar{f} \leq \frac{f_0}{1 + \frac{b}{M^2}}[1 + (e^{b/M^2} - 1)e^{-M\eta}], \tag{101}$$

where, for Model II the coefficients are

$$a = E\beta h_0, \quad b = \beta h_0(E - h_0/\lambda), \quad M = (E\beta\lambda)^{1/2}, \quad m = [\beta(E\lambda - h_0)]^{1/2},$$

and for Model IV the coefficients are $a = E\beta\lambda_2 h_0$, $b = h_0\beta\lambda_2(E - \frac{h_0}{\lambda_1})$, $M = [E\beta\lambda_1\lambda_2]^{1/2}$, $m = [\beta\lambda_2(E\lambda_1 - h_0)/(1 + h_0)]^{1/2}$ and $h_0 = h(0)$. Using the same coefficients the bounds

$$h_0\, e^{-M\eta} \leq h(\eta) \leq h_0\, e^{-m\eta} \tag{102}$$

can also be derived for both cases. Then the bounds for $g(\eta)$ follow from the conservation law as

$$\underline{g}(\eta) = E - \bar{h}/\lambda \leq g(\eta) \leq E - \underline{h}/\lambda = \bar{g}(\eta) \qquad (103)$$

for Model II, and

$$\underline{g}(\eta) = E\lambda_2 - \frac{\lambda_2}{\lambda_1}\bar{h}(\eta) \leq g(\eta) \leq E\lambda_2 - \frac{\lambda_2}{\lambda_1}\underline{h}(\eta) = \bar{g}(\eta) \qquad (104)$$

for Model IV.

Many upper and lower bounds for Models I-IV were computed for a range of the parameters. These are shown in Table I. While not always of uniform accuracy they do remarkably well and are usually very accurate for the pollutant. It should be remarked again that these are not coupled but are computable independently. Consequently, if one is interested only in the pollutant only that bound needs to be computed.

TABLE I

BOUNDS FOR TRAVELLING WAVE SOLUTIONS

f = pollutant
g = bacteria (obtained by conservation law)
h = carbon

A) Model I,II (All bounds at $\eta = 0.1$)

Parameters				Model I		Both Models		Model II	
ε	β	λ	h(0)	$\underline{f}$	$\overline{f}$	$\underline{h}$	$\overline{h}$	$\underline{f}$	$\overline{f}$
1	10	10	1	0.729	0.741	0.368	0.381	0.937	0.946
1	10	10	.1	0.729	0.730	0.0368	0.0369	0.993^-	0.994
1	100	100	.1	0.3679	0.3680	0.454×10^{-5}	0.456×10^{-5}	0.999^-	0.999^+
10	100	10	9	0.0423	0.0489	0.00041	0.00055	0.442	0.499
10	10	10	9	0.368	0.385	0.381	0.419	0.464	0.517
10	100	10	90	0.04	0.368	0.004	0.161	0.406	0.471
10	10	100	100	0.368	0.387	0.0045	0.0064	0.406	0.471
10	100	100	100	0.0423	0.0498	0	0	0.406	0.471

B) Model III,IV (All bounds at $\eta = 0.02$)

Parameters					Model III		Both Models		Model IV	
ε	β	λ_1	λ_2	h(0)	$\underline{f}$	$\overline{f}$	$\underline{h}$	$\overline{h}$	$\underline{f}$	$\overline{f}$
1	10	10	10	1	0.819	0.827	.531	.619	0.951	0.96
1	10	10	100	.1	0.819	0.820	.053	.054	0.995	0.99
1	100	10	10	.1	0.531	0.533	.0135	.0145	0.995	0.99
1	100	100	100	.9	0.135	0.137	0	0	0.985	0.99
10	10	100	10	100	0.135	0.150	0	.00014	0.529×10^{-5}	0.47
10	100	10	10	10	0.135	0.150	.0179	.910	0.058	0.54
10	10	100	100	1	0.1353	0.1355	0	0	0.981	0.99
10	100	10	100	10	0.135	0.150	0.018	.910	0.034	0.49

10. THE STEADY STATE

Now we treat the steady state case for all four models and obtain upper and lower bounds on the solutions. The details will be given for two cases and the results stated for the remaining two. The steady state is found by setting $\frac{\partial C_i}{\partial t} \equiv 0$, $i = 1,2,3$ and then we shall write $C_1 = p(x)$, $C_2 = q(x)$ and $C_3 = r(x)$ to distinguish these results from travelling wave solutions. Equations (1), (2), (3) then reduce to

$$-\frac{d^2p}{dx^2} + \beta \frac{dp}{dx} + \beta\phi(p,q,r) = 0 \tag{105}$$

$$-\frac{d^2q}{dx^2} + \beta \frac{dq}{dx} - \beta\lambda_2\psi(q,r) = 0 \tag{106}$$

$$-\frac{d^2r}{dx^2} + \beta \frac{dr}{dx} + \beta\lambda_1\psi(q,r) = 0, \tag{107}$$

where

	Model I	Model II	Model III	Model IV
$\phi(p,q,r)$	pq	pqr	pq	pqr
$\psi(p,q)$	qr	$(\lambda_2 = 1)$	$\frac{qr}{1+r}$	"Monod kinetics"

10.1 Bounds for the Pollutant (p)

In both Models I and III the equation

$$-p'' + \beta p' + \beta pq = 0 \tag{108}$$

holds with the boundary conditions $p(0) = p_0 > 0$, $\lim_{x\to\infty} p' = 0$ and the (physical) assumption $p(x) > 0$ for all $x \geq 0$. From the conservation laws $q = A - r/\lambda$ for Model I and $q = A\lambda_2 - \lambda_2 r/\lambda_1$ for Model III we again get $\lim_{x\to\infty} q(x) = A$ for Model I, and $\lim_{x\to\infty} q(x) = A\lambda_2$ for Model III.

The first derivative can be eliminated in (108) by setting $P = e^{-\beta x/2} p$ whereupon (108) becomes

$$-P'' + (\beta^2/4 + \beta q)P = 0 \tag{109}$$

with $P(0) = p(0) = p_0$. The behavior of $P(x)$ as $x\to\infty$ can easily be shown to have the property that $\lim_{x\to\infty} P(x) = 0$. Bounds are developed for equation (109) and then transformed back to $p(x)$.

For Model I we introduce the comparison problems

$$\begin{aligned} &-\overline{P}'' + [\beta^2/4 + \beta(A - \frac{r_0}{\lambda})]\overline{P} = 0,\ \overline{P}(0) = \overline{P}_0,\ \lim_{x\to\infty} \overline{P}(x) = 0 \\ &-\underline{P}'' + [\beta^2/4 + A\beta]\underline{P} = 0,\ \underline{P}(0) = p_0,\ \lim_{x\to\infty} \underline{P}(x) = 0 \end{aligned} \tag{110}$$

where $r_0 = r(0)$. These have solutions

$$\begin{aligned} \overline{P} &= p_0 \exp\{-\tfrac{1}{2}[\beta(\beta + 4(A - r_0/\lambda))]^{1/2} x\} \\ \underline{P} &= p_0 \exp\{-\tfrac{1}{2}[\beta(\beta + 4A)]^{1/2} x\}. \end{aligned} \tag{111}$$

For Model III the comparison problem is

$$-\bar{P}'' + [\beta^2/4 + \beta\lambda_2(A - r_0/\lambda_1)]\bar{P} = 0,\ \bar{P}(0) = p_0,\ \lim_{x\to\infty} \bar{P}(x) = 0$$

$$-\underline{P}'' + [\beta^2/4 + A\beta\lambda_2]\underline{P} = 0,\ \underline{P}(0) = p_0,\ \lim_{x\to\infty} \underline{P}(x) = 0$$

whose solutions are

$$\bar{P} = p_0 \exp\{-\tfrac{1}{2}[\beta(\beta + 4\lambda_2(A - r_0/\lambda_1))]^{1/2} x\}$$

$$\underline{P} = p_0 \exp\{-\tfrac{1}{2}[\beta(\beta + 4A\lambda_2)]^{1/2} x\} \qquad (112)$$

By the maximum and minimum principles we have again that $\underline{P} \le P \le \bar{P}$ for all $x \ge 0$. Finally by means of $p(x) = e^{\beta x/2}P$ the bounds

$$\bar{p}(x) = p_0 \exp \tfrac{x}{2}\{\beta - [\beta(\beta + 4(A - r_0/\lambda))]^{1/2}x\}$$

$$\underline{p}(x) = p_0 \exp \tfrac{x}{2}\{\beta - [\beta(\beta + 4A)]^{1/2}\} \qquad (113)$$

are obtained for Model I, such that $\underline{p}(x) \le p(x) \le \bar{p}(x)$ for all $x \ge 0$. For Model III the results are

$$\bar{p}(x) = p_0 \exp \tfrac{x}{2}\{\beta - [\beta(\beta + 4\lambda_2(A - r_0/\lambda_1))]^{1/2}\}$$

$$\underline{p}(x) = p_0 \exp \tfrac{x}{2}\{\beta - [\beta(\beta + 4A\lambda_2)]^{1/2}\}. \qquad (114)$$

These bounds like those for f in Section 8 can be used independently of the other components. Of course they all involve the parameters of the problem and the initial data.

For Models II and IV the corresponding results are

$$p(x) \le \bar{p}(x) \le \tilde{p}(x) = \frac{p_0}{1 + \frac{b}{m(m+\beta)}} \left[1 + (e^{b/m^2} - 1)e^{-mx}\right]$$

where $m = -\frac{1}{2}\{\beta - [\beta(\beta + 4A\lambda)]^{1/2}\}$, $b = r_0\beta(A - \frac{r_0}{\lambda})$ for Model II,

$$m = -\frac{1}{2}\{\beta - [\beta(\beta + 4A\lambda_1\lambda_2)]^{1/2}\}, \quad b = r_0\beta\lambda_2(A - \frac{r_0}{\lambda_1}) \text{ for Model IV,}$$

which furnish the upper bounds. The lower bounds are given by

$$p(x) \ge \underline{p}(x) \ge \underset{\sim}{p}(x) = p_0 e^{-a/M^2}\left(1 + \frac{a}{M(M+\beta)} e^{-Mx}\right)$$

where

$$M = -\frac{1}{2}\{\beta - [\beta(\beta + 4(A\lambda - r_0)]^{1/2}\}, \quad a = A\beta r_0 \text{ for Model II,}$$

$$M = -\frac{1}{2}\{\beta - [\beta(\beta + 4\lambda_2 \frac{A\lambda_1 - r_0}{1 + r_0})]^{1/2}\}, \quad a = A\beta\lambda_2 r_0 \text{ for Model IV.}$$

Because the original bounds $\underline{p}$ and $\bar{p}$ involve complicated Bessel functions they are not solved but estimates are given using their properties.

10.2 Bounds for the Active Carbon (r)

The equations for r(x) in the steady state case of each model are

$$\begin{aligned} -r'' + \beta r' + \beta(A\lambda - r)r &= 0 \text{ for Models I and II,} \\ -r'' + \beta r' + \beta\lambda_2 \left(\frac{A\lambda_1 - r}{1+r}\right) r &= 0 \text{ for Models III and IV,} \end{aligned} \tag{115}$$

with $r(0) = r_0 > 0$ and $\lim_{x\to\infty} r' = 0$ in all cases. From phase plane analysis we can show that $\lim_{x\to\infty} r(x) = 0$ with r monotone decreasing since $0 < r(x) \le r_0 < A\lambda_1$. The condition $r_0 < A\lambda_1$ implies the uniqueness of the solution.

Since a maximum, minimum principle holds for equations of the form

$$-y'' + ay' + by = 0,\ y(0) = 0,\ y \to 0 \text{ as } x \to \infty$$

comparison equations are set up for (115) with the following results:

For Models I and II (For m and M use the appropriate values from Section 10.1)

$$r_0 e^{-mx} = \underline{r} \leq r(x) \leq \bar{r}(x) = r_0 e^{-Mx} \tag{116a}$$

For Models III and IV (For m and M use the appropriate values from Section 9.1)

$$r_0 e^{-mx} = \underline{r} \leq r(x) \leq \bar{r}(x) = r_0 e^{-Mx} \tag{116b}$$

Both results hold on $0 \leq x < \infty$.

A sample of bounds is shown in Table II for a range of the parameters. These bounds are independently computable.

TABLE II

BOUNDS FOR STEADY STATE SOLUTIONS

p = pollutant
q = bacteria
r = carbon

A) Models I,II (all bounds at x = 0.1)

Parameters				Model I		Both Models		Model II	
A	B	λ	r_0	$\underline{p}$	$\bar{p}$	$\underline{r}$	$\bar{r}$	$\underline{p}$	$\bar{p}$
1	10	10	1	.912	.920	.539	.564	.954	.960
1	100	10	9	.906	.990	3.60	8.15	.455	.948
1	10	100	.1	.9124	.9125	.00671	.00672	$.9991^+$	$.9991^+$
10	10	10	1	.539	.541	.067	.068	.912	.914
10	10	10	10	.539	.564	.671	.787	.430	.490
10	10	100	100	.539	.564	.007	.012	.403	.468

B) Models III,IV (all bounds at x = 0.02)

Parameters					Model III		Both Models		Model IV	
A	B	λ_1	λ_1	h(0)	$\underline{p}$	$\bar{p}$	$\underline{r}$	$\bar{r}$	$\underline{p}$	$\bar{p}$
1	10	10	10	1	.884	.892	.583	.715	.943	.964
1	10	10	100	1	.583	.602	.149	.287	.862	.928
1	10	100	10	.1	.8837	.8838	.015	.016	.99908	.99915
10	100	100	10	1	.290	.291	$.4\times10^{-7}$	$.7\times10^{-5}$	.980	.990
10	100	100	100	9	.0045	.0046	0	0	.465	.916
10	100	10	10	1	.291	.293	.0045	.028	.828	.908

11. INTERVAL ANALYSIS

In the previous two sections bounds upon the solutions were obtained which involved the parameters of the problems in various ways. In many practical problems the exact values of parameters, such as biokinetic rate constants, turbulent diffusivity etc, may not be known except on some interval - i.e. $\underline{\beta}<\beta<\overline{\beta}$ which is written as $\beta \in [\underline{\beta},\overline{\beta}]$ in interval notation. Interval analysis will be used, together with the bounds of Sections 9,10 to provide information about the solutions when the parameters are known only on intervals. This appears to be a better line of attack than treating the system statistically when the probability distributions are unknown. The details of interval analysis and interval arithmetic may be found in Moore [15,16] and Adams [17]. The method is illustrated for the upper bound on r(x) (see equation (116b)

$$\overline{r}(x) = r_0\{\exp \frac{x}{2}[\beta - (\beta^2 + 4\beta\lambda_2(A\lambda_1 - r_0))^{1/2}]\},$$

where it is assumed that $A > 0$ and $r_0 = r(0)$ are positive fixed numbers, with $A\lambda_1 > r_0$.

For convenience we introduce the notation $\rho = \overline{r}/r_0$, $\gamma = \beta - (\beta^2 + 4\beta\lambda_2(A\lambda_1 - r_0))^{1/2}$ so that $\rho = e^{x\gamma/2}$. The interval analysis is carried out under the assumption that β, λ_1, and λ_2 are independent for every $\beta \in [\underline{\beta},\overline{\beta}]$ and for every $\lambda_i \in [\underline{\lambda}_i,\overline{\lambda}_i]$ $(i=1,2)$

such that $\underline{\beta}$, $\underline{\lambda}_i > 0$, $\underline{A\lambda}_i > r_0$. Choose any fixed $\beta_0 \in [\underline{\beta},\overline{\beta}]$, $\lambda_{i0} \in [\underline{\lambda}_i,\overline{\lambda}_i]$, for example $\beta_0 = \underline{\beta} + \frac{\beta-\underline{\beta}}{2}$, $\lambda_{i0} = \underline{\lambda}_i + \frac{\overline{\lambda}_i - \underline{\lambda}_i}{2}$. An outer approximation of the range of $\rho(x;\beta, \lambda_1,\lambda_2)$ for every $\beta \in [\underline{\beta},\overline{\beta}]$ and for every $\lambda_i \in [\underline{\lambda}_i,\overline{\lambda}_i]$ (i=1,2), with $x > 0$, is to be determined. In particular, an upper bound $\overline{\rho}$ of this range, will be constructed.

Since ρ is a complicated function of β, λ_1, λ_2 a crude bound $\overline{\rho}_0$ can be obtained via the interval evaluation

$$\rho(x,\beta,\lambda_1,\lambda_2) \in \exp\{\tfrac{x}{2}([\underline{\beta},\overline{\beta}] - ([\underline{\beta}^2,\overline{\beta}^2] + 4[\underline{\beta\lambda}_2(\underline{A\lambda}_1-r_0),\overline{\beta\lambda}_2(\overline{A\lambda}_1-r_0)])^{\frac{1}{2}})\}$$

that is $\rho \in [\underline{\rho}_0(x),\overline{\rho}_0(x)]$ where

$$\overline{\rho}_0(x) = \exp\{\tfrac{x}{2}(\overline{\beta} - (\beta^2 + 4\beta\lambda_2(A\lambda_1 - r_0))^{\frac{1}{2}})\} \text{ for } x > 0 \qquad (117a)$$

and

$$\underline{\rho}_0(x) = \exp\{\tfrac{x}{2}(\underline{\beta} - (\overline{\beta}^2 + 4\beta\lambda_2(A\lambda_1 - r_0))^{1/2})\} \text{ for } x > 0 \qquad (117b)$$

But, since $\underline{\beta}$ and $\overline{\beta}$ both appear $\overline{\rho}_0$ does not belong to the set of admitted functions for ρ. An upper envelope (lower envelope) is constructable by using the maximum of $\gamma = \gamma(\beta,\lambda_1,\lambda_2)$ for fixed x and for every

$$(\beta,\lambda_1,\lambda_2) \in [\underline{\beta},\overline{\beta}] \otimes [\underline{\lambda}_1,\overline{\lambda}_2] \otimes [\underline{\lambda}_1,\overline{\lambda}_2] \equiv I \subset \mathbb{R}^3. \qquad (118)$$

Instead of the direct interval evaluation of $\overline{\rho}_0$, given by (117a), a deferred interval evaluation of the first order will be constructed. For this purpose ρ will be represented by a

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* $\otimes$ is used to indicate the set product.

Taylor-polynomial with a remainder term of the first order, for fixed $x > 0$, and with $\gamma_0 = \gamma(\beta_0, \lambda_{10}, \lambda_{20})$, $z = (\beta, \lambda_1, \lambda_2)$, $z_0 = (\beta_0, \lambda_{10}, \lambda_{20})$ as the point of expansion. This expansion is

$$\rho(x,z) = \rho(x,z_0) + (\beta-\beta_0)\ \partial\rho(x,z_0+\theta)/\partial\beta + \tag{119}$$

$$+ (\lambda_1-\lambda_{10})\partial\rho(x,z_0+\theta)/\partial\lambda_1 + (\lambda_2-\lambda_{20})\partial\rho(x,z_0+\theta)/\partial\lambda_2,$$

with $\theta(x,z,z_0) \in (0,1)$ for every $z \in I$ and fixed x. Since <u>θ is not known</u> the partial derivatives have to be replaced by the range of these functions for every $z \in I$ with x fixed. This range is not known so <u>intervals</u> must be constructed which contain the range of these functions:

$$\rho(x,z) \in \rho(x,z_0) + (\beta-\beta_0)\left[\underline{\frac{\partial\rho}{\partial\beta}}, \overline{\frac{\partial\rho}{\partial\beta}}\right] + (\lambda_1-\lambda_{10})\left[\underline{\frac{\partial\rho}{\partial\lambda_1}}\ ,\ \overline{\frac{\partial\rho}{\partial\lambda_1}}\right]$$

$$+ (\lambda_2 - \lambda_{20})\left[\underline{\frac{\partial\rho}{\partial\lambda_2}}, \overline{\frac{\partial\rho}{\partial\lambda_2}}\right] \tag{120}$$

for every $z \in I$ and $x > 0$ fixed. The bounds of these intervals are x dependent and $\underline{\frac{\partial\rho}{\partial\beta}}$ ($\overline{\frac{\partial\rho}{\partial\beta}}$) stands for the lower (upper) bounds of an interval to be constructed which contains the range of $\frac{\partial\rho}{\partial\beta}$ for every $z \in I$ and x fixed.

The bounds for the derivatives of ρ are obtained from an interval evaluation of those derivatives in the following form*.

*The designation A=:B means B is defined by A.

$$\frac{\partial\rho}{\partial\beta}=\frac{\partial}{\partial\beta}\,e^{\gamma x/2}=\frac{x}{2}\,e^{\gamma x/2}\,\frac{\partial\gamma}{\partial\beta}=\frac{x}{2}\,e^{\gamma x/2}\left(1-\frac{2\beta+4\lambda_2(A\lambda_1-r_0)}{2\sqrt{\beta^2+4\beta\lambda_2(A\lambda_1-r_0)}}\right)$$

$$\epsilon\left\{\exp\frac{x}{2}\,([\underline{\beta},\overline{\beta}]-\sqrt{[\underline{\beta}^2,\overline{\beta}^2]+4[\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1-r_0),\overline{\beta}\overline{\lambda}_2(A\overline{\lambda}_1-r_0)]}\right\}\frac{x}{2}\left\{1-\right.$$

$$\left.-\frac{[\underline{\beta},\overline{\beta}]+2[\underline{\lambda}_2(A\underline{\lambda}_1-r_0),\overline{\lambda}_2(A\overline{\lambda}_1-r_0)]}{\sqrt{[\underline{\beta}^2,\overline{\beta}^2]+4[\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1-r_0),\overline{\beta}\overline{\lambda}_2(A\overline{\lambda}_1-r_0)]}}\right\}=:[\underline{\frac{\partial\rho}{\partial\beta}},\overline{\frac{\partial\rho}{\partial\beta}}] \qquad (121)$$

where

$$\underline{\frac{\partial\rho}{\partial\beta}}=\left\{\exp\frac{x}{2}(\underline{\beta}-\sqrt{\overline{\beta}^2+4\overline{\beta}\overline{\lambda}_2(A\overline{\lambda}_1-r_0)}\right\}\frac{x}{2}\left\{1-\frac{\overline{\beta}+2\overline{\lambda}_2(A\overline{\lambda}_1-r_0)}{\sqrt{\underline{\beta}^2+4\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1-r_0)}}\right\} \qquad (122a)$$

$$\overline{\frac{\partial\rho}{\partial\beta}}=\left\{\exp\frac{x}{2}(\overline{\beta}-\sqrt{\underline{\beta}^2+4\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1-r_0)}\right\}\frac{x}{2}\left\{1-\frac{\underline{\beta}+2\underline{\lambda}_2(A\underline{\lambda}_1-r_0)}{\sqrt{\overline{\beta}^2+4\overline{\beta}\overline{\lambda}_2(A\overline{\lambda}_1-r_0)}}\right\} \qquad (122b)$$

$$\frac{\partial\rho}{\partial\lambda_1}=\frac{\partial}{\partial\lambda_1}\,e^{\gamma x/2}=\frac{x}{2}\,e^{\gamma x/2}\,\frac{\partial\gamma}{\partial\lambda_1}=-\frac{x}{2}\,e^{\gamma x/2}\,\frac{4A\beta\lambda_2}{2\sqrt{\beta^2+4\beta\lambda_2(A\lambda_1-r_0)}} \qquad (123)$$

$$\frac{\partial\rho}{\partial\lambda_2}=\frac{\partial}{\partial\lambda_2}\,e^{\gamma x/2}=\frac{x}{2}\,e^{\gamma x/2}\,\frac{\partial\gamma}{\partial\lambda_2}=-\frac{x}{2}\,e^{\gamma x/2}\,\frac{4\beta(A\lambda_1-r_0)}{2\sqrt{\beta^2+4\beta\lambda_2(A\lambda_1-r_0)}} \qquad (124)$$

There follows

$$\underline{\frac{\partial\rho}{\partial\lambda_1}}=\frac{x}{2}\left\{\exp\frac{x}{2}(\overline{\beta}-\sqrt{\underline{\beta}^2+4\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1-r_0}\right\}\left\{\frac{(-2)A\overline{\beta}\overline{\lambda}_2}{\sqrt{\underline{\beta}^2+4\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1-r_0)}}\right\}, \qquad (125a)$$

$$\overline{\frac{\partial\rho}{\partial\lambda_1}}=\frac{x}{2}\left\{\exp\frac{x}{2}(\underline{\beta}-\sqrt{\overline{\beta}^2+4\overline{\beta}\overline{\lambda}_2(A\overline{\lambda}_1-r_0)}\right\}\left\{\frac{(-2)\underline{\beta}\underline{\lambda}_2A}{\sqrt{\overline{\beta}^2+4\overline{\beta}\overline{\lambda}_2(A\overline{\lambda}_1-r_0)}}\right\} \qquad (125b)$$

and corresponding results for $\overline{\partial\rho}/\partial\lambda_2$ and $\partial\rho/\underline{\partial\lambda_2}$. Using equations (120) to (125) the following bounds for ρ are obtained:

$\rho(x,z) \in [\underline{\rho}_1(x), \bar{\rho}_1(x)]$ where

$$\bar{\rho}_1(x) = \rho(x,z_0) + (\beta-\beta_0)\begin{cases}\overline{\frac{\partial\rho}{\partial\beta}} & \text{if } \beta>\beta_0 \\ \underline{\frac{\partial\rho}{\partial\beta}} & \text{if } \beta\le\beta_0\end{cases} + (\lambda_1-\lambda_{10})\begin{cases}\overline{\frac{\partial\rho}{\partial\lambda_1}} & \text{if } \lambda_1>\lambda_{10} \\ \underline{\frac{\partial\rho}{\partial\lambda_1}} & \text{if } \lambda_1\le\lambda_{10}\end{cases}$$

$$+ (\lambda_2-\lambda_{20})\begin{cases}\overline{\frac{\partial\rho}{\partial\lambda_2}} & \text{if } \lambda_2>\lambda_{20} \\ \underline{\frac{\partial\rho}{\partial\lambda_2}} & \text{if } \lambda_2\le\lambda_{20}\end{cases} \qquad (126)$$

and

$$\underline{\rho}_1(x) = \rho(x,z_0) + (\beta-\beta_0)\begin{cases}\overline{\frac{\partial\rho}{\partial\beta}} & \text{if } \beta>\beta_0 \\ \underline{\frac{\partial\rho}{\partial\beta}} & \text{if } \beta\le\beta_0\end{cases} + (\lambda_1-\lambda_{10})\begin{cases}\overline{\frac{\partial\rho}{\partial\lambda_1}} & \text{if } \lambda_1>\lambda_{10} \\ \underline{\frac{\partial\rho}{\partial\lambda_1}} & \text{if } \lambda_1\le\lambda_{10}\end{cases}$$

$$+ (\lambda_2-\lambda_{20})\begin{cases}\overline{\frac{\partial\rho}{\partial\lambda_2}} & \text{if } \lambda_2>\lambda_{20} \\ \underline{\frac{\partial\rho}{\partial\lambda_2}} & \text{if } \lambda_2\le\lambda_{20}\end{cases}. \qquad (127)$$

All the equations (117a), (122)-(125) reveal that the interval $I \in \mathbb{R}^3$ (see (118)) must be small enough so that

$$\bar{\beta}-[\underline{\beta}^2 + 4\underline{\beta}\underline{\lambda}_2(A\underline{\lambda}_1 - r_0)]^{1/2} < 0 \qquad (128)$$

Equation (128) is <u>not</u> a consequence of $\beta-[\beta^2+4\beta\lambda_2(A\lambda_1-r_0)]^{1/2} < 0$ for every $z \in I$. If (128) does not hold the expressions for the upper bounds $\bar{\rho}_0$ and $\bar{\rho}_1$ will contain exponentials with positive exponents. These become unbounded as $x\to\infty$ and are therefore not admissible.

This process, in which ρ is represented by a Taylor-polynomial with a remainder, can be continued to higher order terms - e.g. to second order. The interval evaluation of the second derivative $\partial^2\rho/\partial\beta^2$ and the other five derivatives of second order can be done but the calculation becomes more and more difficult as the order of differentiation increases. The increasing complexity of those expressions causes the interval evaluations of the respective remainder terms to yield overestimates of the ranges of the derivatives.

It is therefore recommended to use the approximate bounds given by (126) and (127). If necessary these can be computed separately for sufficiently many points of expansion, $z_0^{(m)} \in I_m$ such that $I = \bigcup_{m=1}^{N} I_m$, where I_m are each sufficiently small for the approximations to be meaningful.

Remark 10: It is observed that the following attempt at an approximation of the range of ρ for every $z \in I$ often yields rather inaccurate results. Let $\rho(x,z)$ be computed for x fixed at fixed vectors $z^{(n)} \in I$, $n=1,2,\cdots,9$. Then $\overline{\rho}$, (or $\underline{\rho}$) is taken to be the largest (smallest) of the computed values $\rho^{(n)}$. There is no error estimate for this approximation. The inaccuracy is due to the fact that even many different random generations of the $z^{(n)}$ do not ensure that the range of ρ can be approximated thusly.

12. SUMMARY AND CONCLUSIONS

(a) For four kinetic models of stirred-tank type dimensional analysis has been applied, dimensionless kinetic groups obtained and analytic solutions developed and analyzed. In the case of Model II (third order kinetics for C_1, second order for C_2 and C_3) the dimensionless equations are also parameter free. This is an interesting and somewhat unusual situation. From an examination of these exact solutions the following limiting results (as $t \to \infty$) are obtained:

Model Number	C_1	C_2	C_3
I	0	$\neq 0$	0
II	$\neq 0$	$\neq 0$	0
III	0	$\neq 0$	0
IV	$\neq 0$	$\neq 0$	0

From the exact solutions for the oft-used Model I, it is shown in Section 4 how these equations can be used to obtain rate constant ratios and the individual rate constants.

(b) When transport effects (constant velocity) are included, the resulting first order hyperbolic partial differential equations must be dimensionally analyzed in a manner different from the kinetic models. This is done and exact solutions are developed in

all four cases. It is further demonstrated that the same analysis can be applied when the velocity depends upon the spatial (x) coordinate. In principle, there is no difficulty in extending this analysis to three spatial dimensions.

(c) When turbulent dispersion effects are included, the equations become coupled reaction-diffusion equations which are parabolic. Dimensional analysis reveals the importance of the reciprocal of a Peclet number for mass transport and reaction rate ratios. None of the model equations possess classical similar solutions. But, they all possess traveling wave solutions. For Models I and II a partial exact solution is constructed which can be used to generate a perturbation solution for the pollutant. Both show the subtle way the problem parameters enter. In particular, the pollutant decays according to the exponential of the negative of the square root of the term $N_{Pe}E$ and by a complicated function of $\lambda = k_3/k_1$ (see equation 87) for Model I)). On the other hand, the active carbon decays according to the exponential of the negative of the square root of $N_{Pe}Ek_3/k_1$ (see equation (84)).

(d) The complicated functions experienced in the perturbation analyses suggested that upper and lower bounds be constructed in terms of simple functions (negative exponentials, here). This has been done for all travelling wave solutions in Section 9 and for the steady state in Section 10. Those bounds may be used independently! That is they are not coupled together. Moreover, the bounds show

how the various parameters effect the solutions. This is the most useful and interesting result to come out of this work.

(e) Since none of the parameters are known exactly interval analysis has been used in Section 11 to give deferred interval bounds in which the upper bound lies.

Some of the results are verified by computer calculations.

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